A STUDY OF SOME FACTORS UNDERLYING THE PRODUCTION OF ALLOYS BY DIFFUSION IN THE SOLID STATE

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J. Paton Cranston, B.Sc.(Glasgow),
A.R.T.C.,
Department of Metallurgy,
Victoria University,
Manchester.

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CHAPTER I

INTRODUCTION

In this research a survey of some of the factors affecting the production of alloys from mixed powdered metals was undertaken with the object of gaining a better understanding of the mechanism of alloying and of binding of the particles which may occur at temperatures below the melting points of both metals or of any phase in the binary system formed by the two metals.

The work was mainly restricted to the copper-zinc system, but when data had been obtained for this system under a given set of conditions, substitution of other metals for either copper or zinc gave confirmatory evidence of mechanism of alloying suggested by the results of this research.

For the most part the progress of diffusion and sintering was followed indirectly by observing certain changes of physical properties as they occurred during the heating of compressed discs of the mixed powdered metals.

The changes in microstructure were noted, but owing to the unfamiliarity of the structures obtained with powder metallurgical specimens, particular care had to be taken in interpreting the structures. On this point X-ray powder photographs were particularly useful in confirming the identity

of a phase observed under the microscope. On the other hand X-ray methods of analysis suffer from one serious limitation; they do not enable the distinction to be made between lattice distortions due to chemical inhomogeneity and lattice distortions which arise from cold-working during compression and persist up to the recrystallization temperature.

Dimensional changes were observed with a dilatometer and travelling microscope. It was found that these changes were a particularly sensitive guide to the progress of diffusion.

Measurements of the variations of electrical resistance and mechanical strength of the discs were used in this work mainly to indicate the physical changes at the points of contact of the compacted particles.

The change in the solubility of zinc under standard conditions after partial diffusion and thermal analyses helped to disclose the nature of the chemical changes occurring during diffusion.

The results are detailed and discussed individually in Chapter V. They are further discussed collectively in Chapter VI in the light of a possible explanation of the process of alloying in the solid state when certain pairs of powdered metals are compressed and heated.

It is thought that the essential feature of this method of alloying is that one of the metals should have a high vapour pressure. When this condition is fulfilled the volatile component is transported to the other by continuous distillation and condensation. This implies that alloying is more rapid at a given temperature than might be expected if solid diffusion across the interface of the particles were the rate controlling process.

It is believed that homogeneous alloys of such pairs of metals might be formed at much lower temperatures than are used commercially to-day.

CHAPTER II

PREVIOUS EXPERIMENTAL WORK RELEVANT TO THIS RESEARCH

A review of the literature on the production of alloys from powdered metals reveals work chiefly of a technological nature. Some of the few more fundamental papers are reviewed here.

In order to standardize some of the variables met with in powder metallurgy it is desirable that the pressure distribution throughout the compact should be as uniform as possible.

Seelig and Wulff[1] investigated the variation of effective pressure with distance from the face of the plunger transmitting the pressure. The method employed was to measure the density of successive layers of compressed powder. The true pressure on these layers was determined by equating these densities with the densities of very thin compacts pressed at known pressures. When nickel was subjected to an external pressure of 30 tons per sq.inch a linear relationship was found between the effective pressure and the depth below the plunger face:-

$$P_E = P_T \left(1 - \tfrac{2}{3} d\right)$$

where P_E = effective pressure in tons/sq.in. at a depth d inches below the plunger face.

P_T = applied pressure in tons/sq.in.

Thus at a depth of 0.1 inch the effective pressure was about 6% less than the applied pressure. The reduction in effective pressure is due in part to the resistance of the material to plastic deformation and in part to friction at the die wall. If, as seems possible, both these effects are dependent on, among other factors, the tensile strength of the material, it is reasonable that the reduction in effective pressure in copper-zinc compacts will be less due to the tensile strength of both copper and zinc being lower than that of nickel.

In this present work 10 gram samples were used for all experiments except for those on thermal analyses. This weight yielded a disc compact 1.13 inches in diameter and 0.1 inch deep. The above work by Seelig and Wulff indicates that the effective pressure throughout a compact of this size would be within a few per cent. of the applied pressure.

Owen and Pickup[2] investigated the interdiffusion of zinc and copper. They did so by heating uncompacted samples of mixed filings in evacuated glass tubes to temperatures between 450°C. and 600°C. for periods up to

200 hours. The course of diffusion was followed by examining X-ray photographs of the diffusion-treated samples. It was inferred that diffusion was very nearly complete when the lines due to the beta phase had disappeared, the alpha doublet had become resolvable, and the parameter corresponded to the parameter of the normally cast and annealed alloy of the same composition.

They concluded that diffusion occurred more rapidly when finely divided powders were used than when coarser powders were used and that "interdiffusion takes place, in reasonable time, only when the temperature of diffusion is above the melting point of zinc" (419.4°C.).

Kirkendall[3] calculated the rate of diffusion of zinc out of brass into copper by electroplating copper onto a cylinder of 60/40 brass and heating the composite specimen to 780°C. for 1 to 701 hours. By examining successive thin layers of metal by X-ray diffraction he was able to determine the percentage of zinc in each layer and the concentration gradient. Using Ficks Law[4] the value they calculated for the diffusion co-efficient for zinc in 26% brass is D 3.8×10^{-9} sq.cm./sec. at 780°C.

In this work he discovered what is now known as the "Kirkendall Effect" - that is, the shifting of the interface between two metals that are interdiffusing. This

arises from the differences in the diffusion co-efficients of the two metals. In this case the interface moved outwards the copper owing to the zinc diffusing into the copper faster than the copper diffuses into the brass.

Constance Elam[5] heated copper rods in an atmosphere of zinc vapour. The zinc condensed on the copper to form the beta and gamma brass phases, no alpha phase was observed separating beta from the original copper when the temperature was below 450°C. Above 450°C. alpha and beta were observed. The rods were observed to increase in diameter 300-400% in forming gamma.

H. E. Hall[6] heated to 810°C. compacts containing 84.6% copper, 9.4% tin, 6% graphite, after pressing at 60,000 p.s.i. Microsections prepared after heating for 1 to 30 minutes showed the progressive diffusion of the tin into the copper, forming initially high tin phases. After 25 - 27 minutes the specimens appeared to be chemically homogeneous alpha bronze. The porosity was observed to increase with sintering time but no explanation was advanced. He noted that "completely alloyed bronzes may be obtained from powders at much lower temperatures (than 810°C.), perhaps even those below the melting point of tin" (231°C.).

C. G. Goetzel[7] Sintered Copper - Zinc Compacts at 600°C. and 800°C. While mainly interested in obtaining

optimum mechanical properties he noted a volume expansion, in some cases approaching 50%. This was attributed to:-

"(a) Release of stresses originating from cold pressing.

(b) Gas adsorption and entrapped air at room temperature and gas evolution at elevated temperatures.

(c) Shrinkage caused by sintering, diffusion, grain growth, gravity forces, creep, etc.

The volume increase with rising zinc content may be explained on the basis that the zinc constituent, having a large surface, gives off a large amount of zinc vapour at the sintering temperature."

It is felt by the present author that, since the vapour pressure of zinc is less than 0.1 atmosphere at 800°C., its vapour could not directly cause the expansion.

In a recent paper Duwez and Martens[8] review the dilatometric study of the sintering of metal powder compacts. In the case of copper-zinc compacts they found an abnormal expansion between 300 and 700°F. This they attributed to the "mass transfer of zinc into copper during diffusion". They justify this on the grounds that zinc is soluble in copper, whereas copper is practically insoluble in zinc.

CHAPTER III

THEORIES OF DIFFUSION AND SINTERING

Once the existence of diffusion in the solid state had been confirmed, Fick[9] gave a theory of diffusion based on the analogous phenomenon of thermal conductivity:-

$$M = -AD\frac{dc}{dx} \qquad (1)$$

where M is the quantity of material diffusing in unit time through an area A when the concentration gradient in a direction normal to A is $\frac{dc}{dx}$. D is the diffusion co-efficient, a constant at a given temperature.

This equation has to be modified for non-steady states to:-

$$\frac{dc}{dt} = \frac{d}{dx}(D\frac{dc}{dx}) \qquad (2)$$

It was shown by Matano[10] that D varied markedly in some cases with concentration. It can be shown by thermodynamic reasoning that the activity gradient $\frac{\partial a}{\partial x}$ should be substituted for the concentration gradient. If this were done D would be a constant, independent of the activity gradient, but owing to the lack of knowledge of activities it is usual to keep the form (2) and determine experimentally the variation of D with concentration.

The variation of D with temperature is given by the Dushman-Langmuir equation[11]

$$D = D_o e^{E/RT}$$

where E, the activation energy is a constant, and D_o is a constant independent of temperature.

The form of this equation can be justified for ideal solutions by considering diffusion as an atomic "barrier" phenomenon. On theoretical grounds both E and D_o vary with temperature, but over the ranges of temperature normally met with the variation is less than experimental errors.

Three mechanisms for internal diffusion have been suggested.

(1) Diffusion by mutual interchange of two neighbouring atoms, which must be of a different species in order to lead to observable diffusion. This mechanism necessitates the equal rate of diffusion of the two species and so cannot account for the Kirkendall effect.

(2) Diffusion of one species through holes in the lattice of the other. These holes may arise through dislocations, mosaic structures or other lattice imperfections, or they may be lattice vacancies. The number of these vacancies (Schottky defects) has been calculated by Mott and Gurney[12] and by Barrer[13] from thermodynamic theory. Calculation of rates of

diffusion by this mechanism leads to values of D of the same order as experimentally determined rates.

(3) Diffusion through interstitial space. (Frenkel defects.) This is of importance where one species has a very much smaller atomic radius than that of the matrix. This mechanism is of importance when hydrogen and carbon diffuse in iron.

THEORIES OF SINTERING.

Sintering is most usually defined as the increase in density resulting from the mechanical and heat-treatment of a body of solid particles.

This increase in density causes other physical and chemical changes in the powder; the mechanical properties and electrical and thermal conductivities normally improve due to the greater effective cross-sectional area or to larger contact areas between the particles. Those chemical properties which are a function of the surface energy of the particles, such as adsorption, electrode, potential, etc. decrease, due to the decrease in total surface energy.

The equilibrium state for a solid body is a single particle with minimum surface energy. For an isotropic material this would be a sphere and for an anisotropic material it would be a regular crystal. The "driving force"

which tends to sinter an aggregate of powder is the decrease in free energy of the system which results from the disappearance of solid-solid and solid-gas interfaces.

That a small particle has a higher free energy than a large particle of the same material in the same condition has been well known for some time. That it is true of powder metals also has been shown by Price, Smithells and Williams,[14] who observed that in "heavy" metal compacts of W, Cu, and Ni, the smaller particles of Tungsten dissolved in the liquid matrix and redeposited on larger particles of W. This shows that the smaller particles of Tungsten possess a greater solubility and consequently a higher free energy than larger particles.

Huttig[15] calculated the change in free energy per gm-atom in forming a single crystal of gold from cubic particles of different edge lengths

edge length	F cals/gm atom
10^{-4} cms.	-36.93
10^{-5} cms.	-369.3
10^{-6} cms.	-3693

This surface free energy will be greater for more electronegative elements, when of high purity, such as copper and zinc. In practice the observed surface free energy would be less than for the metal in the highly pure condition, due to adsorbed gases on the surface of the particles.

The effect of raising the temperature of a group of particles can be considered in two parts. Firstly, the surface free energy is altered, due to changes in the total surface area by diffusion and due to the adsorption and evolution of gases. Secondly, the mobility of the atoms increases. The second effect alone will cause an increase in the rate of approach to the equilibrium state. The first effect may partly oppose this increase.

Huttig, as a result of extensive study of the surface properties of fifteen elements and compounds, finds that there are four stages in the behaviour of the surface during heating. He defines a ratio (alpha) as the absolute temperature under consideration divided by the absolute melting point of the particular element or compound.

alpha	
up to .23	Gas evolution greater than expected by temperature alone - due in part to removal of voids.
.23 - .36	All-round increase in surface activity, due to degassing.
.33 - .45	Deactivation of surface, due to surface diffusion.
.37 - .53	Activation, due to lattice diffusion.

Huttig's work leads to a picture of the thermo-

dynamic forces operating in such a way as to bring an aggregate of powder to the equilibrium solid state.

Rhines[16] (communication to paper by Shaler, A.I.M.E., Vol.185, 1949) reports on some work done on the mechanism of densification. Pore counts indicate that as sintering progresses in a compact the largest pores increase in size and number while the smallest pores disappear. Densification progresses by the adsorption of small pores by large pores in the interior and by the atmosphere at the surface. The mechanism of this adsorption is by the diffusion of Schottky defects (lattice vacancies) from near the smaller pores to larger pores and to the surface. The number of these defects is greater round the smallest pores than elsewhere, so that there exists a concentration gradient down which the defects can diffuse. Birchenall[16] has calculated the rate of densification and the change in pore size by such a process and finds agreement with the observed data.

In a recent seminar on the Kinetics of Sintering[17] Shaler suggests that the mechanism of sintering is by viscous flow of the material into the pores of a compact under the impetus of surface tension (gamma)

$$\text{where} \quad \gamma = \frac{\delta F}{\delta S} \qquad \text{(I)}$$

and $\frac{\delta F}{\delta S}$ is the rate of change of free energy with change in surface area.

Gibbs[18] has shown that surface tension on a curved surface separating two phases is equivalent to a pressure (P) perpendicular to the surface

$$P = \frac{2\gamma}{r} \qquad \text{(II)}$$

where r radius of curvature of the surface.

Shaler considers that material moves into or out of a pore until the radius of curvature of the pore is such that the pressure difference between the entrapped gas and the atmosphere is equal to the pressure given by (II).

Convincing evidence is given of the importance of entrapped gases in the sintering of powders. Compacts which had obtained a constant density after heating in a nitrogen atmosphere were observed to expand when the nitrogen was evacuated and replaced by 0.5 mm. pressure of hydrogen. This expansion he attributes to the compact readjusting itself until the pressure difference once again equals the pressure given in (II).

Kuczynski[19] showed mathematically that the contact area$^{(x)}$ of two spheres in contact at constant temperature should be a function of the time depending on the sintering mechanism as follows:-

Viscous or plastic flow	$x^2 \propto T$
Evaporation and condensation	$x^3 \propto T$
Volume diffusion	$x^5 \propto T$
Surface diffusion	$x^7 \propto T$

He found experimentally that the fifth power proportionality expressed his results most closely in the case of large particles (greater than 15μ). In the case of small particles (less than 15μ) and at the beginning of all sizes the seventh power was a closer approximation.

Thus Kuczynski's results suggest that volume diffusion is predominant in the sintering of large particles. No increase in porosity of the particles was observed during the reinforcement of the area of contact, so that the net effect of the process is the transfer of material from the surface of the particle to the contact area. Why such a process should procede at a rate characterized by volume diffusion is not yet clear. Further experimental work is required for a full understanding of the process.

MacKenzie and Shuttleworth[20] discuss the theories of sintering advanced by Kuczynski and Shaler, and develop a mathematical treatment calculated on the assumption that crystalline materials behave as Bingham solids. With regard to Kuczynski's ideas they calculate that the decrease in linear dimensions by volume and surface diffusion would be very much less than is observed in practice. Further, if these mechanisms were the only

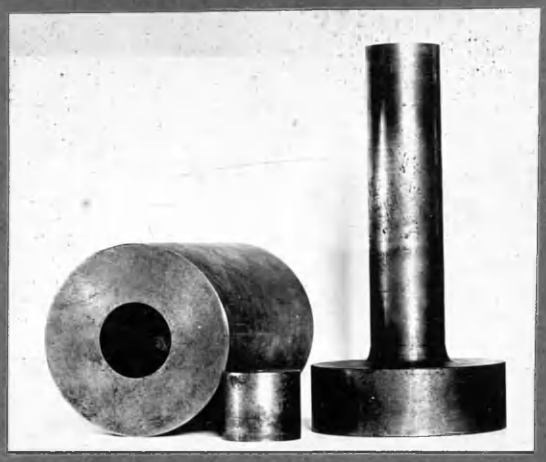
operative ones, densification would occur first at the surface and move inwards. They conclude that volume diffusion is not the operative mechanism.

With regard to Shaler's ideas they point out that metals, even at temperatures near their melting points, will have a yield point, and so behave more like a Bingham solid where flow only occurs above the yield point. Shaler assumes that metals at elevated temperatures behave as Newtonian viscous solids having no yield point.

MacKenzie and Shuttleworth, like Shaler, assume that the force causing sintering is surface tension, but point out that at a critical distance from a pore the shear stress arising from surface tension at that pore surface will be less than the yield shear stress. If this critical distance does not lie within the critical distance of an other pore then densification will be impossible.

They calculated the rate of densification where the critical distances overlap for various values of yield shear stress and the rate of densification when the pore contains an indiffusible gas.

The curves they derive of density against time await experimental confirmation.



1

FIGURE 1 DIE AND PLUNGER ASSEMBLY

2

FIGURE 2 INVAR HOLDER

3

FIGURE 3SHOWING SET-UP OF SPECIMEN IN HOLDER

CHAPTER IV

DESCRIPTION OF APPARATUS

The compacts were made in a die and plunger, illustrated in fig.1. The material used was a three inch bar of alloy steel, containing 4.5% Ni, 1.5% Cr, 0.3% C, which gave (after quenching and tempering at 220°C.) a yield point of over 100 tons/sq.in. The cross-sectional area of the die was 1 sq.in. The plunger was made longer than the die in order to facilitate the removal of the compact after compression. Pressures up to 20 tons/sq.in. were applied using an Avery machine; higher pressures were attained with a 100 ton vertical hydraulic press.

After compression the compacts were supported upright in an Invar holder, (Figs.2 and 3) in order to carry out dilatometric heating curves. This holder had two small holes bored down from the top; one to allow a silica rod to rest on the compact, the other to contain a chromel-alumel thermocouple. The hot junction of the couple was less than one-tenth of an inch away from the centre of the compact, thus the errors in temperature measurement due to temperature gradients in the furnace were negligible. The top of the silica rod was sighted

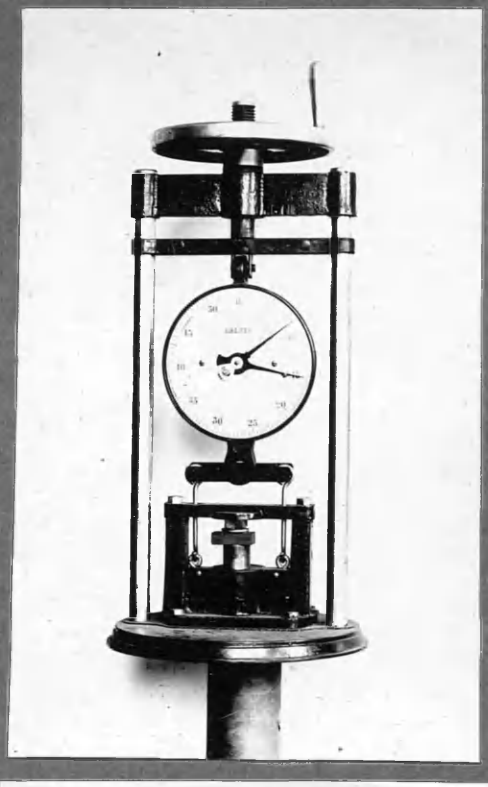


FIGURE 4
B.C.I.R.A. COMPRESSION TESTER

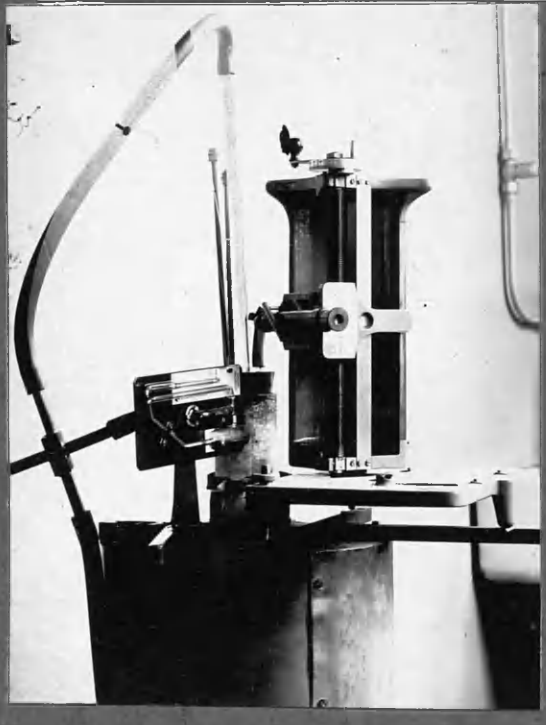


FIGURE 5 FURNACE AND DILATOMETER IN POSITION

at the top of the furnace.

The holder rested on a silica stool which, in turn, rested on the sealed end of a silica furnace tube. An 18 gauge Nichrome V wire was wound round an alundum sleeve which fitted over the silica tube. The power input was regulated by a variac transformer which was hand-operated to give the desired heating rate.

During the experiments the furnace was usually continuously evacuated by a Metrovac rotary pump which was connected to the top of the furnace by thick-walled rubber tubing of half an inch internal diameter. The thickness of this tubing prevented the use of glass T-pieces as junctions. Experiments showed that T-pieces made by soldering copper tubes into a brass block were suitable and accordingly these were used, as shown in fig.9.

The furnace was sealed with a rubber bung which had been fitted with a $\frac{1}{2}$" diam. glass tube and two $\frac{1}{4}$" diam. copper conductors (Fig.6) One of the glass tubes carried the thermocouple leads while the other was connected to the vacuum pump and enabled the top of the silica rod resting on the specimen to be sighted with the cathetometer. (Fig.5) The scale of the cathetometer read directly to .01 of a millimeter and reproducible readings could be obtained for the position of the top of the silica rod to

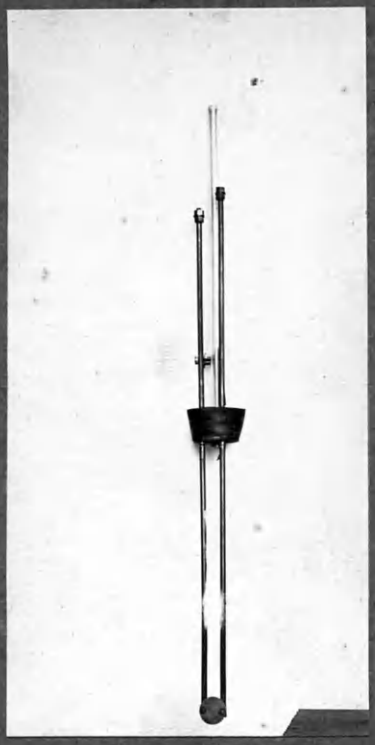


FIGURE 6
COPPER CONDUCTORS
AND SPECIMEN

FIGURE 7 TWO-COMPARTMENT HOLDER

0.003 mm.

In order to measure the resistivity of the compacts, copper conductors held the specimens in the hot zone of the furnace and carried the current for the resistivity determinations. The specimen had two small holes bored in it about $\frac{7}{8}$" apart, which enabled it to be bolted to the copper conductors. The voltage drop across the outside ends of the conductors was measured on a Cambridge Potentiometer. The current could be varied from one to three amperes, according to the initial resistance of the specimen. Owing to the uncertain and possibly slightly varying contact resistances no attempt was made to relate the observed readings to absolute resistivities, nor was it considered valid to compare the resistance of one specimen with another.

It is interesting to note that very good vacuum-tight contact was made between the glass tubes and the rubber bung by boring the holes in the bung using a cork-borer adapted to fit a power-driven drilling machine. This ensured smooth-walled holes which formed effective seals with the glass and with the copper conductors. The vacuum attained was measured by an Edwards vacustat and never exceeded 0.05 mm.

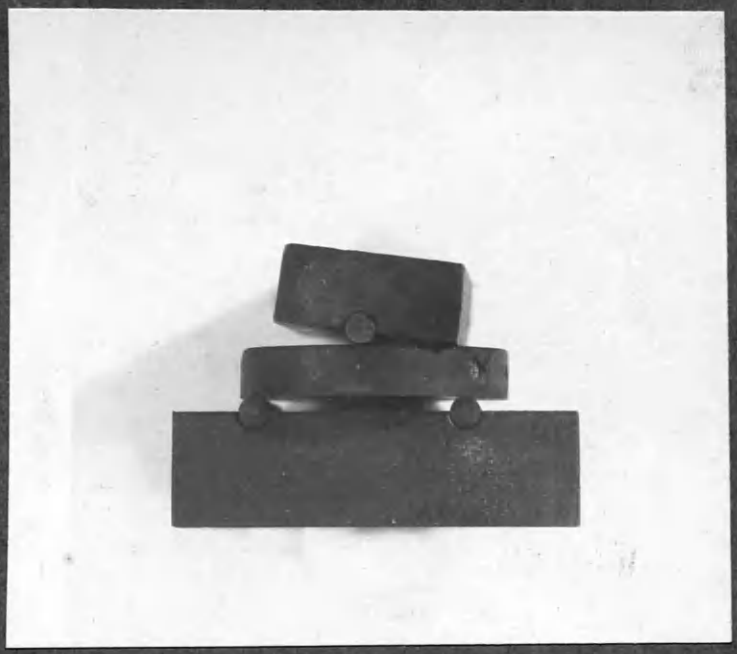


FIGURE 8 SET-UP FOR COMPRESSION TESTING

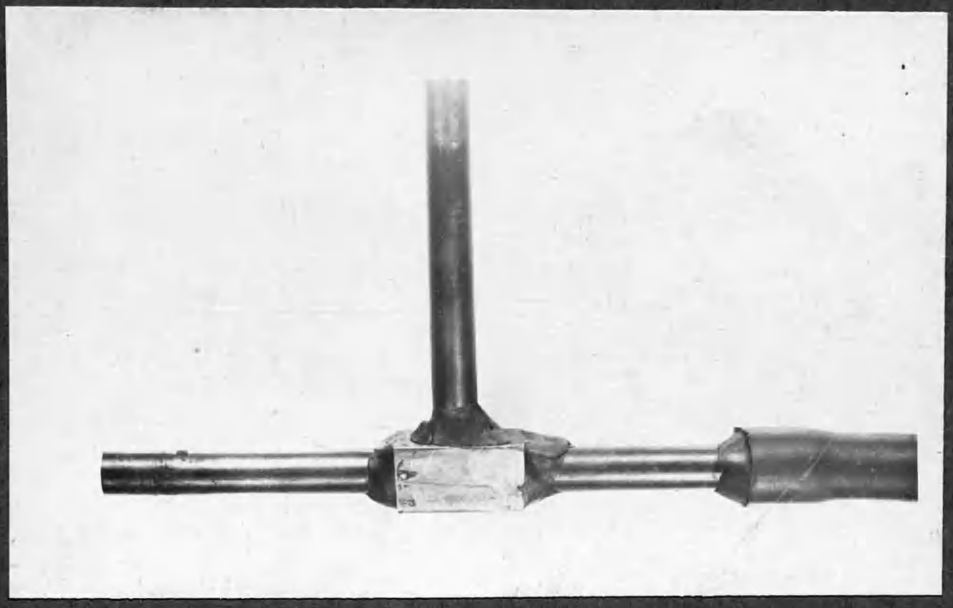


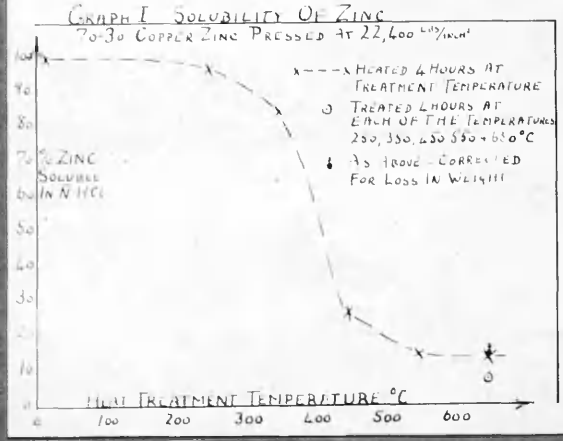
FIGURE 9 COPPER AND BRASS T-PIECE

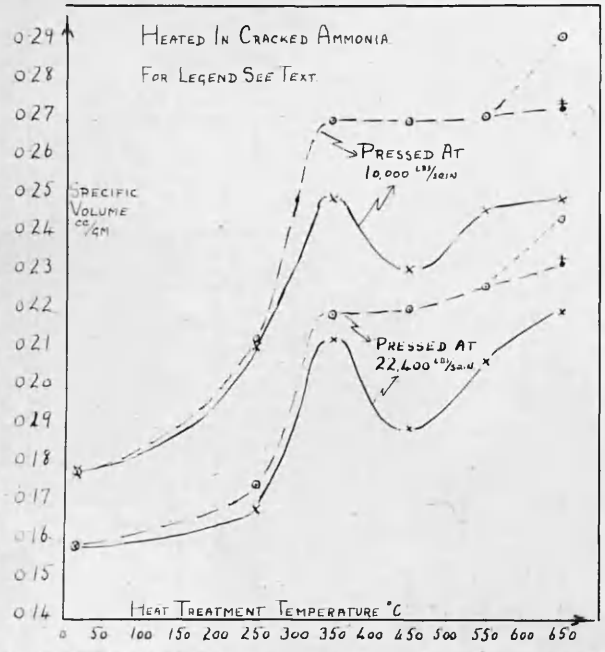
For the thermal analysis a brass two-compartmented holder (fig.5) was made. One compartment contained a 25 gm. neutral body, consisting of a copper powder compact in the case of copper-zinc specimens, or a nickel powder compact in the case of nickel-zinc specimens. In each case the neutral body was pressed at the same pressure as the specimen. The other compartment contained the 25 gm. alloy powder compact. Holes were drilled from the edge of the compacts along the diameter to accommodate the ends of the differential thermocouple. The whole assembly was heated in the evacuated silica furnace.

The strength of the compacts after heat-treatment was determined by breaking them under a slowly applied bend stress applied across the diameter by the assembly shown in fig.8. The load was measured by the B.C.I.R.A. sand compression strength tester shown in fig.4.

TABLE I

Sizing Analysis %			
Mesh		Copper	Zinc
	-52	0.0077	—
-52	-60	0.0138	—
60	-85	0.228	—
-85	-100	1.740	—
-100	-120	7.015	—
-120	-150	11.680	0.452
-150	-170	11.030	2.364
170	-200	0.266	2.586
200	-240	12.500	3.840
-240	-300	8.040	5.646
-300		45.720	83.514





CHAPTER V

EXPERIMENTAL RESULTS, WITH DISCUSSION IN DETAIL

A - RAW MATERIALS

With the exception of the cadmium powder, the powders used in this research were supplied by Powder Metallurgy Ltd., London. The cadmium powder was prepared by filing a rod of pure cadmium. The sizing analyses of the "Electrolytic Copper Powder" and the "S" Grade Zinc Powder" are given in Table I. The nickel powder was all less than 300 mesh. The size of the cadmium filings was undetermined.

B - SOLUBILITY OF ZINC AFTER DIFFUSION TREATMENT

Six compacts were made from 7 gms. of copper and 3 gms. of zinc. The powders were mixed with a spatula on a piece of high gloss paper followed by "tumbling" from one end of the paper to the other. This method of mixing was found to lead to no appreciable segregation when the compacts were examined under the microscope. The powder was then transferred to the die and the plunger brought down on the powder by hand. The plunger was then rotated through several revolutions to spread the powder to a uniform depth; this procedure was found to yield a compact

of uniform thickness and density after pressing. The pressure on each compact was maintained at 10 tons/sq.in. for a standard time of five minutes. The plug was then removed and the compact, measuring 1.13" diam. by 0.1", was pushed right out of the die.

Five of the compacts were heated for four hours at 250°C., 350°C., 450°C., 550°C. and 650°C. respectively in an atmosphere of dry, cracked ammonia. The sixth specimen was treated at each of the above temperatures for four hours. Each treated compact was ground in a mortar and pestle, and the percentage of the zinc which dissolved in ten minutes in normal hydrochloric acid was determined. The results are shown in Graph I.

DISCUSSION

An attempt was made to follow the process of diffusion by determining the solubility of the zinc in copper-zinc compacts after diffusion treatment. The results show a rapid drop in solubility between 250°C. and 500°C., showing that the amount of free zinc decreases rapidly in this temperature range. Since the weight of the specimens did not change by more than three per cent. the decrease in the amount of free zinc was due to diffusion and not to loss of zinc by vaporization.

It is possible that equilibrium is not reached

after an isothermal treatment at 650°C. for four hours because the sixth specimen has a lower solubility. This observation may be in error, since a loss of zinc by volatilization would register as a decrease in soluble zinc. When the soluble zinc in the sixth specimen is recalculated, assuming that all the loss in weight of the compact is due to loss of zinc, the result falls on the curve obtained from the other specimens treated once only. This assumption cannot be wholly justified because isothermal treatment at moderate temperatures actually causes the compacts to gain weight.

A similar series of determination for a pressure of 4.46 tons/sq.in. gave similar results with no systematic differences.

This line of work was discontinued owing to the lack of knowledge about the solubility of zinc in high zinc phases under standard conditions. Further, the volatilization of zinc introduces errors which make it difficult to ascertain with accuracy the beginning and end of the drop in solubility of the zinc.

C - CHANGES IN SPECIFIC VOLUME

It was noticed that the compacts prepared above and heated to above 250°C. showed a considerable expansion.

An attempt was made to determine the variation of specific volume with annealing temperature by the method of displacement of water. The porous nature of the compacts led to difficulties due to infiltration of water during weighing. Coating the compacts with vaseline to inhibit wetting and forming a skin on the surface of the compact with collodion was tried without success.

Results were finally obtained by making accurate measurements of the weight and dimensions of the treated compacts.

Two series of 10 gm., 70/30 copper-zinc were prepared, one series pressed for five minutes at 10,000 lbs./sq.in., the other at 22,400 lbs./sq.in.

Five compacts from each series were treated for four hours in cracked ammonia at 250°C., 350°C., 450°C., 550°C. and 650°C. respectively. The sixth compact of each series was treated for four hours at each of the above temperatures. The specific volumes were determined after each treatment.

The calculated specific volumes are plotted on Graph II. The full lines joining the crosses show the specific volumes of the five compacts given only one four hour treatment. The dashed lines connecting the circles show the observed values after each treatment

for the sixth compact.

A further four series were prepared as before at 22,400 lbs./sq.in. The compositions of each series were:-

A 100% Copper

B 100% Zinc

C 70% Copper, 30% Zinc

D 60% Copper, 40% Zinc

The observations were made at 50°C. intervals from 100°C. to 450°C. and are plotted on Graph III.

DISCUSSION

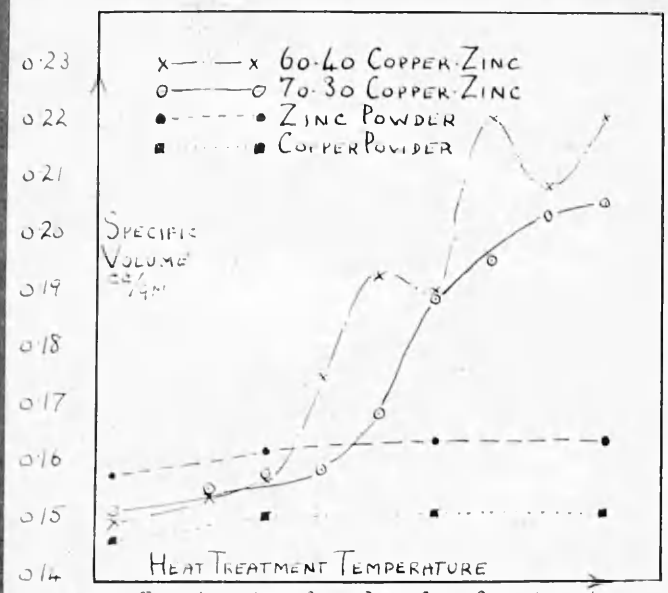
The results show a large increase in specific volume, up to 50%, when an alloy compact is heated to 250°C. and higher. There is no corresponding expansion of the 100% copper or the 100% zinc compacts which at once suggests that the expansion is not caused by an increase in the pressure of entrapped gases within the compact either due to evolution of adsorbed gases or to the expansion of the gases already present. Nor can it be caused by the relief of internal stress. The fact that the 100% zinc compact shows no abnormal expansion confirms that the expansion of the alloy compacts is not caused directly by the vapour pressure of the zinc as suggested by Goetzel.(7)

At this stage in the research the reason for the abnormal expansion was not fully understood. It was clear that it was in some way associated with the diffusion process in spite of the fact that the density of all copper-zinc phases does not vary very greatly from the weighted mean of the density of copper and zinc.

Consideration of the curves for the sixth compact in each series in Graph II (dashed lines) leads to the conclusion that the expansion is substantially complete by 350°C. The increase in specific volume at 650°C. arises from the loss in weight due to dezincification and not due to an increase in dimensions. When the specific volumes are recalculated, ignoring the loss in weight, the values fall into line with the values at 350°C., 450°C. and 550°C. The correction in effect changes the vertical axis of the graph to volume instead of specific volume. The corrected values are shown in the graph thus:-

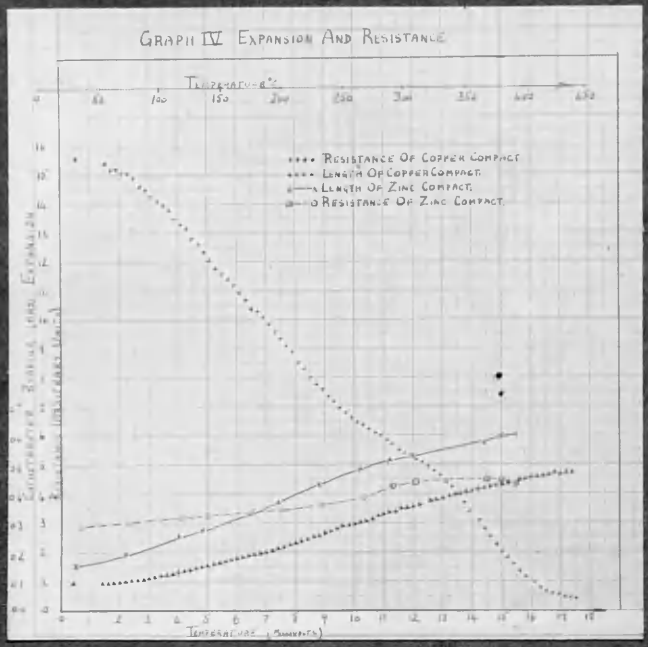
Considering the five compacts in each series diffusion treated only once (full lines in Graph II), it is noticeable that the expansion is less in the case of compacts heated at 450°C. than 350°C. This is likely to arise from the different conditions in the compacts at these two temperatures. At the lower temperature before appreciable diffusion has occurred the compact is an intimate mixture of

Graph III Specific Volume



4 Hours Heating After Pressing At 22,400 Lbs/In²

Graph IV Expansion And Resistance



solid copper and zinc, whereas at the higher temperature there is a mixture of solid copper and liquid zinc.

This method of determining the specific volume was not as accurate as seemed desirable, owing to the friable nature of the compacts leading to inaccuracies in weight, and to the tendency of the compacts to warp leading to inaccuracies in determining the volume. The thinness of the compacts (one-tench inch) meant that the percentage error in measuring the thickness was undesirably large.

To increase the accuracy and to obtain results more easily at smaller intervals of temperature the compacts were heated in a furnace arranged so that continuous dilatometric observations could be made while the specimen was being heated. In no case did the specimen warp nor did the edge of the compact ever crumble in the furnace, so these two sources of error were removed.

D - CHANGE IN LENGTH AND RESISTANCE

i - Single Metal Compacts

The furnace described in Chapter IV for the simultaneous measurement of resistance and length was designed and built in Manchester, as a result of experience in building and modifying two furnaces in Glasgow. Owing to the small scatter of observations due to the high inherent

accuracy of the set-up the individual observations do not appear on the graphs. The points (140-180 per graph) all lie within the thickness of the lines drawn through the points. The observations are recorded in Appendix A.

Except for the observation on the copper-cadmium system the results shown were obtained on the Manchester apparatus.

Using this furnace and the technique earlier described, two 10 gm. compacts of 100% copper and 100% zinc pressed at 20 tons/sq.in. were heated at the rate of 2°C. per minute in a vacuum of less than 0.04 mm. of mercury. The increase in diameter and the change in resistance of the compacts were noted. The current through the copper compact was 1.07 amps. and through the zinc compact it was 3 amps. The observations are plotted in Graph IV.

DISCUSSION

The copper compact increased in length almost linearly with temperature, the increase being 0.375 mm. over 415°C., compared with the theoretical increase of 0.20 mm. calculated from the coefficient of thermal expansion of copper at 40°C. The zinc compact expanded less uniformly, giving a total increase of 0.444 mm., compared with the theoretical value of 0.314 mm.

The difference between the observed and the

theoretical values arises from a combination of circumstances:-

(1) Changes in dimensions arising from the relief of internal stress in the compact.

(2) Changes in dimensions arising from recrystallization of the strained particles.

(3) The expansion of the silica rod and stool.

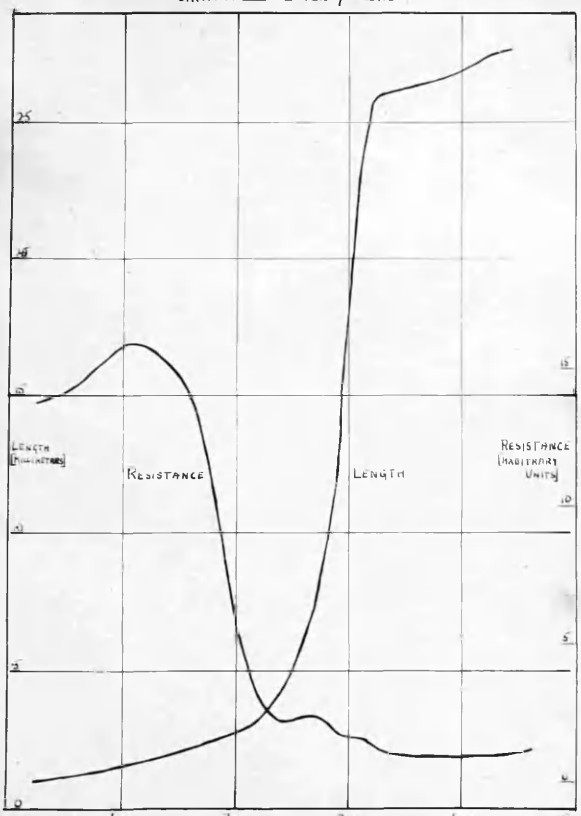
(4) The expansion due to the heating of entrapped gas pockets and to the liberation of absorbed gases.

(5) The contraction associated with the sintering of the particles.

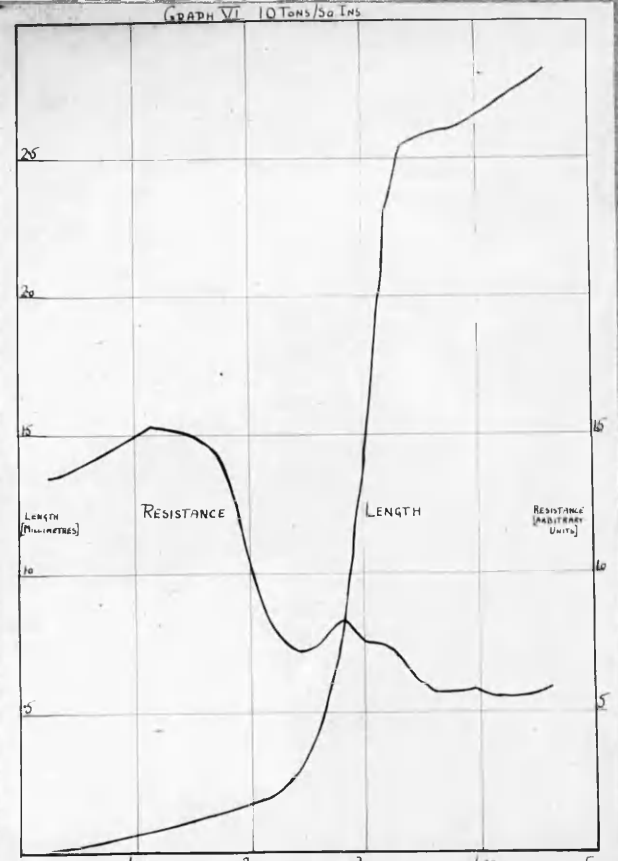
Although the difference between the theoretical and the observed values amounts to about a third of the total expansion in the case of the pure metal compacts, this difference is quite negligible in the case of alloy compacts.

The gradual increase in the electrical resistance of the zinc up to 300°C. is the trend and of the order expected from the temperature coefficient of resistance. Between 20°C. and 220°C. the increase in resistance of the compact due to the temperature coefficient of resistance should be 4.710 units, compared with the experimental increase of 3.605.

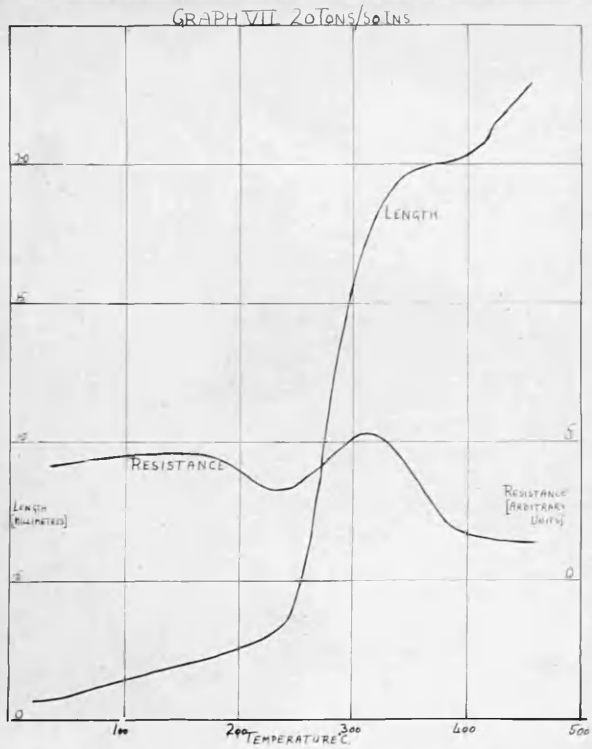
GRAPH V 5 TONS/SQ INS



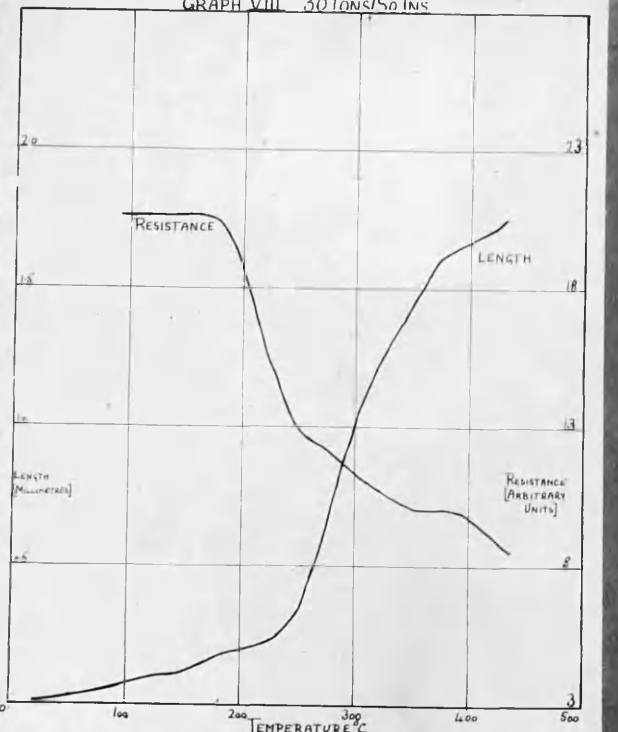
GRAPH VI 10 TONS/SQ INS



GRAPH VII 20 TONS/SQ INS



GRAPH VIII 30 TONS/SQ INS



This discrepancy and the drop in resistance as the melting point of zinc is approached is due to the increase in the area of the points of contact of the particles and to the evolution of adsorbed gases. The contact resistance between the compact and the conductors may also alter.

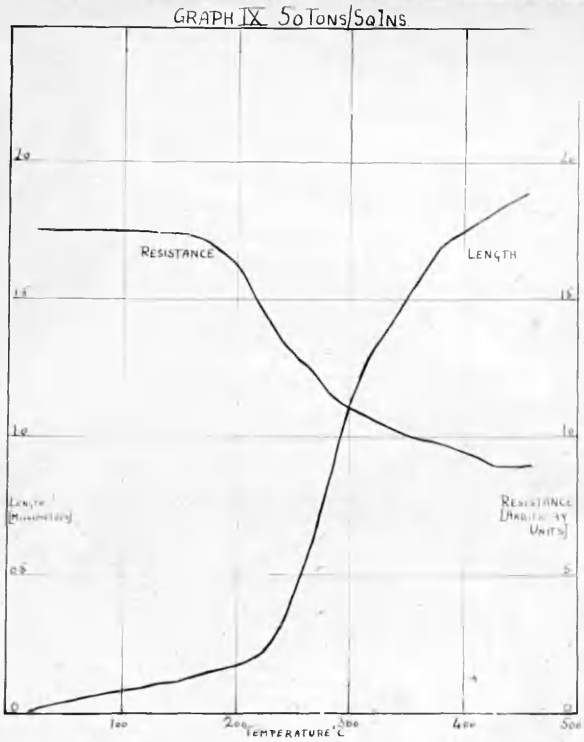
The progressive decrease in resistance of the copper compacts is unexpected. It shows that changes are occurring quite rapidly in compacts at temperatures below 100°C. These changes may be increases in the area of contact between the particles by diffusion or a decrease in the resistance per unit area due to degassing.

It is interesting to note that the initial resistance of the copper is forty-five times the resistance of the zinc. This is due to the different size distribution, total area of contact, yield point and contact resistance between the particles. The resistance of the copper becomes less than the resistance of the zinc above 380°C.

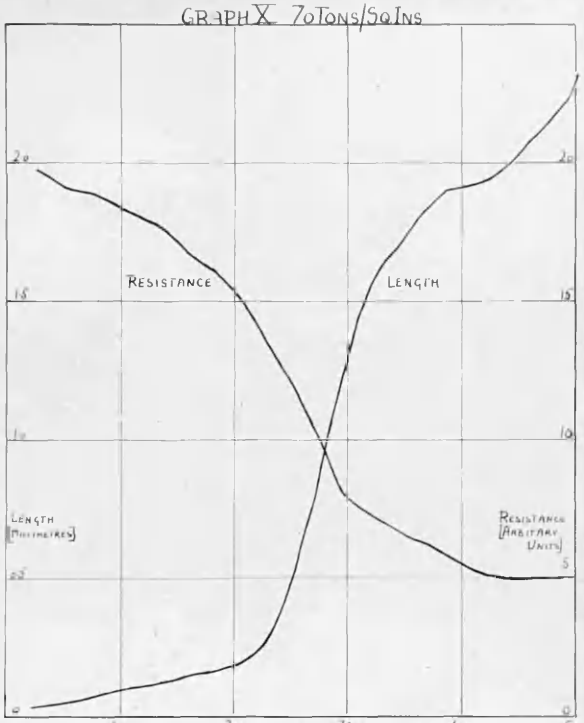
ii - Mixed Powders

Graph V shows a typical plot of the dilation and resistance changes occurring during the heating of a mixed powder compact. In this case the compact was made from 7 gms. of copper and 3 gms. of zinc pressed for 5 minutes

GRAPH IX 50 TONS/SQ INS



GRAPH X 70 TONS/SQ INS



at 5 tons/sq.in. The heating rate was 2°C. per minute.

DISCUSSION

The graph shows a linear expansion up to about 200°C. then a rapid expansion in the range 200°C. to 315°C. Above 315°C. the expansion is more uniform, being near to that calculated from the coefficient of expansion of brass.

The resistance shows firstly an expected increase with temperature. Between 105°C. and 220°C. the resistance decreases rapidly as the contact areas increase and the contact resistances decrease due to degassing and sintering of the particles. At 230°C., the temperature corresponding to the rapid expansion, the resistance increases slightly. Above 260°C. the resistance once again decreases.

It was at this stage in the work that a possible explanation of the phenomen was considered. It was thought that the zinc transferred to the copper particles much faster than the copper moved into the zinc. Thus the original copper particles increased in mass and volume and caused the whole compact to expand. Voids would be left where the zinc originally existed free. For quantitative treatment a simple picture of a compact composed of uniform spheres of copper in contact and the spaces in between filled with zinc was visualized; the zinc was allowed to transfer to the copper spheres and expand them uniformly in all directions. For a

TABLE II

Pressure tons/sq.in.	Temperature of Beginning of "Abnormal Expansion"	Temperature of end of "Abnormal Expansion"	Total "Abnormal Expansion"	Expansion 20°C.-190°C.	Range of "Abnormal Expansion"	Rate of "Abnormal Expansion"	Initial Resistance (Relative)
5	216°C.	324°C.	2.31 mm.	.171 mm.	108°C.	.021 mm/°C.	31.5 units
10	215°C.	332°C.	2.27 mm.	.162 mm.	117°C.	.019 mm/°C.	4.53 units
20	226°C.	346°C.	1.69 mm.	.180 mm.	120°C.	.014 mm/°C.	4.155 units
30	200°C.	385°C.	1.32 mm.	.170 mm.	185°C.	.007 mm/°C.	4.130 units
50	200°C.	(385°C.)	1.50 mm.	.160 mm.	185°C.	.0080mm/°C.	3.510 units
70	179°C.	(385°C.)	1.72 mm.	.145 mm.	206°C.	.0085mm/°C.	6.57 units

70/30 copper-zinc compact the linear expansion calculated from such a picture is 14%. This compares with 7-10% observed on 70/30 copper-zinc compacts compressed at different pressures.

The method by which the zinc was transferred could not be ascertained, but the possibility of distillation was considered.

On the basis of this explanation the increase in resistance between 230°C. and 260°C. is to be explained in two ways:- firstly, by the increase in resistivity when pure copper is alloyed with zinc; secondly, by the disappearance of copper-zinc contacts, which had been acting as conductors.

ii-a - Effect of Varying the Compacting Pressure

A series of six compacts was made of 70/30 copper-zinc powders and pressed at pressures varying from 5 to 70 tons/sq.in. Dilatometric and resistance measurements were made at 5°C. intervals while heating at 2°C./minute in the vacuum furnace.

The observations are plotted on graphs V to X.

Table II (opposite) summarizes the salient features of the graphs.

DISCUSSION

(1) - Dilatometric Curves

As the compacting pressure increases the temperature at which the abnormal expansion first becomes apparent is lowered. This is in keeping with the fact that at higher pressures the particles are in closer contact as shown by relative resistances. This closer contact will cause an appreciable amount of diffusion to occur at a lower temperature.

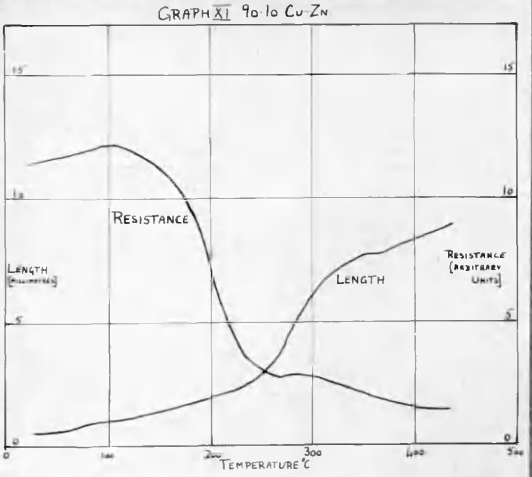
Both the rate of "abnormal" expansion and the total expansion are less with higher compacting pressures. The temperature range over which the abnormal expansion takes place increases with compacting pressure.

These observations cannot be explained at the present stage of the research, but may be bound up with the relative rates of evaporation and diffusion of zinc and the possible loss of zinc by the compact.

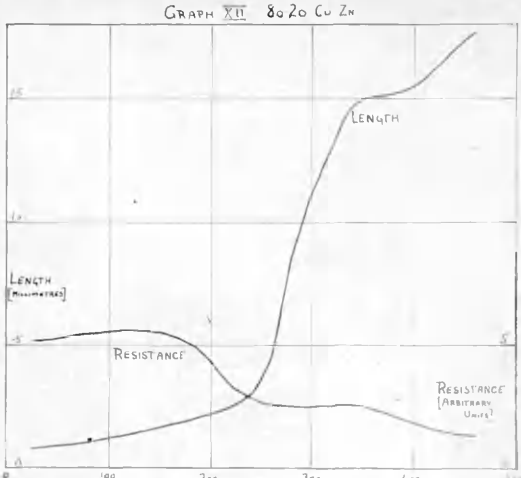
(2) - Resistance Curves

It will be seen that the initial resistance decreases as the compacting pressure increases. It is noticeable that the drop in resistance is lease marked at a pressure of 20 tons/sq.in. than at either higher or lower pressures.

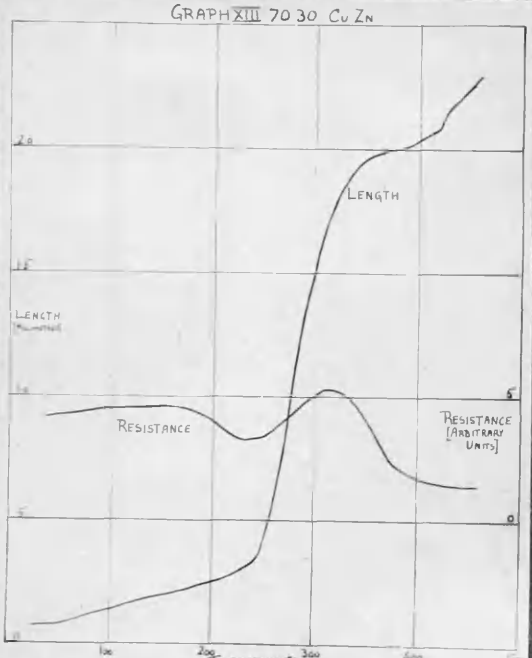
GRAPH XI 90·10 Cu·Zn



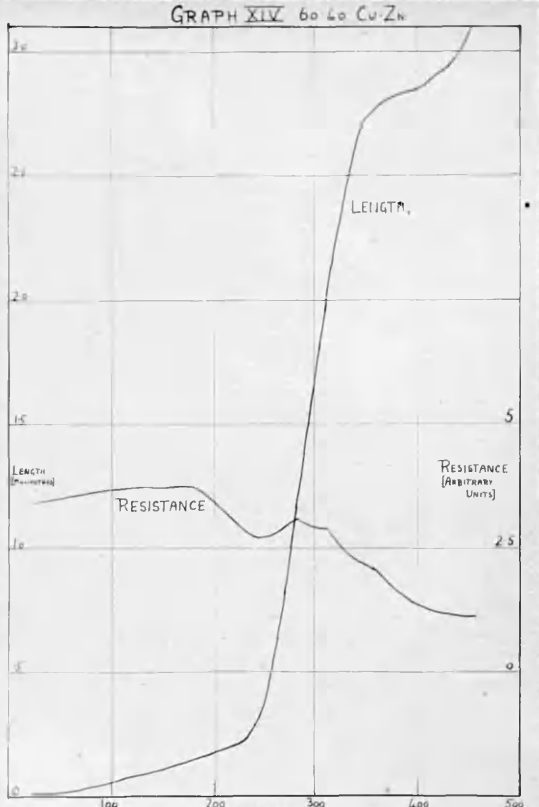
GRAPH XII 80 20 Cu Zn



GRAPH XIII 70 30 Cu Zn



GRAPH XIV 60 40 Cu·Zn



The intermediate increase in resistance is also most marked at a pressure of 20 tons/sq.in. In the case of higher pressures the effect appears only as a change in the rate of decrease of resistance.

No explanation of these observations can be offered yet.

ii-b - Effect of Varying the Percentage of Zinc

A series of six compact were made of copper and zinc powders at 20 tons/sq.in. The compacts contained 10% to 60% of zinc. The dilation and resistance curves obtained while heating at 2C°/min. are shown in graphs XI to XVI.

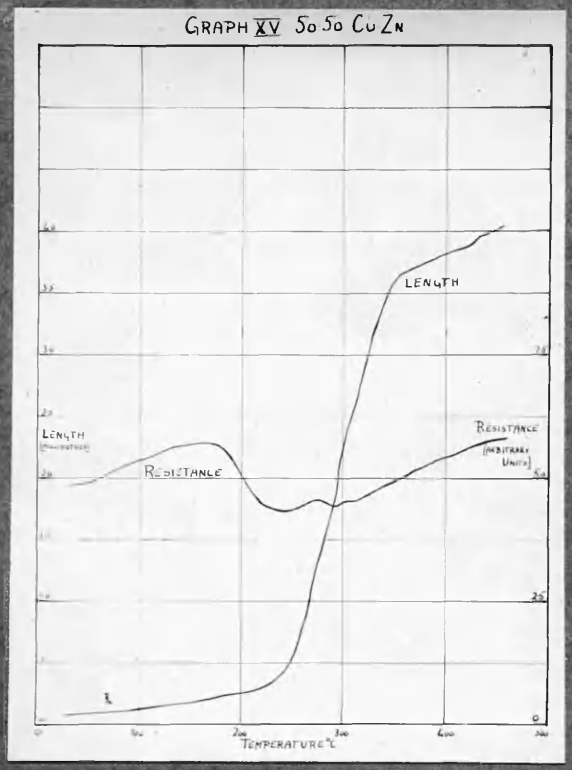
DISCUSSION

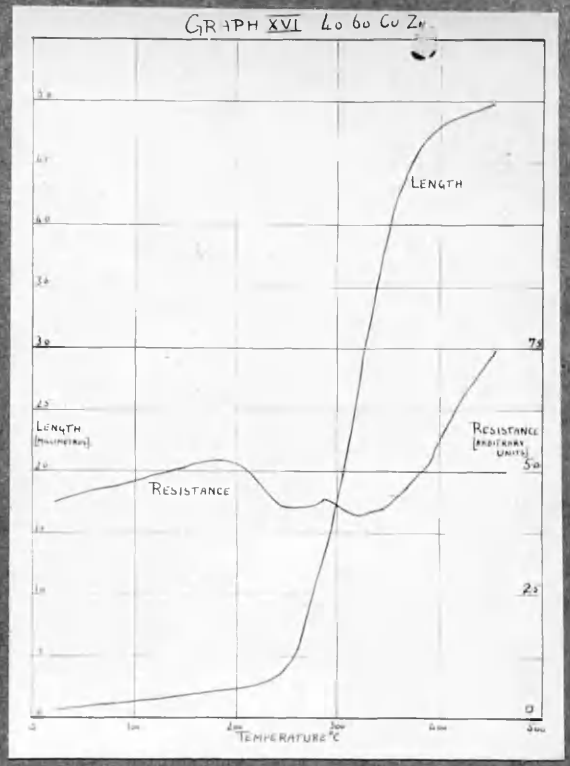
(1) - Dilation Curves

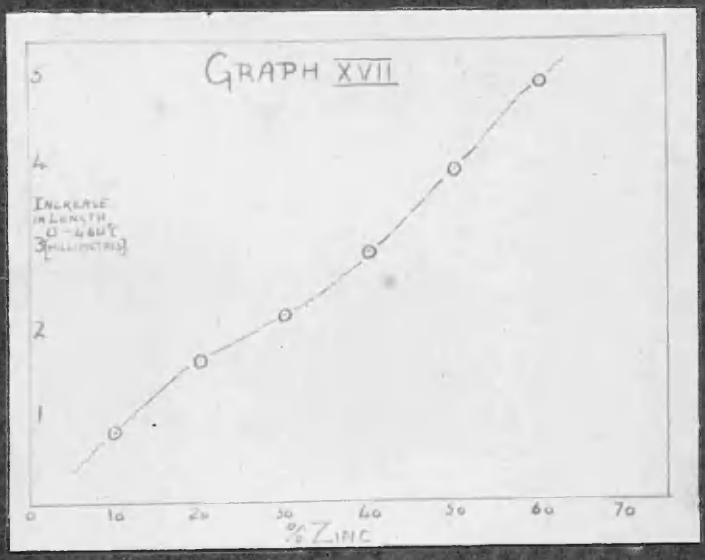
The dilation curves all show the same general character, the magnitude of the abnormal expansion increasing with zinc content. Graph XVII shows the total expansion plotted against composition. The curve is nearly linear passing through the origin. This is in keeping with the hypothesis advanced earlier and confirms that the expansion is actually due to zinc and is proportional to the amount of zinc.

(2) - Resistance Curves

The resistance curves also show the same general


GRAPH XV 50 50 Cu Zn
LENGTH
RESISTANCE
LENGTH
RESISTANCE
(ARBITRARY UNITS)
RESISTANCE
TEMPERATURE °C


GRAPH XVI 40 60 Cu Zn
LENGTH
LENGTH
RESISTANCE
(ARBITRARY UNITS)
RESISTANCE
TEMPERATURE °C


GRAPH XVII
INCREASE IN LENGTH 0-460°C
% ZINC

features, except that with higher zinc contents the resistance increases instead of decreases as the temperature rises above 320°C. This may be attributed to the increase in resistance consequent on alloying of the copper being greater, in the case of high zinc contents, than the decrease in resistance accompanying the fritting of the particles. Above the temperature at which the abnormal expansion ceases the microstructure shows no free zinc, so this increase in resistance is not due to the disappearance of zinc-copper interfacial conductances.

ii-c - Effect of Replacing the Copper and the Zinc Separately and Together

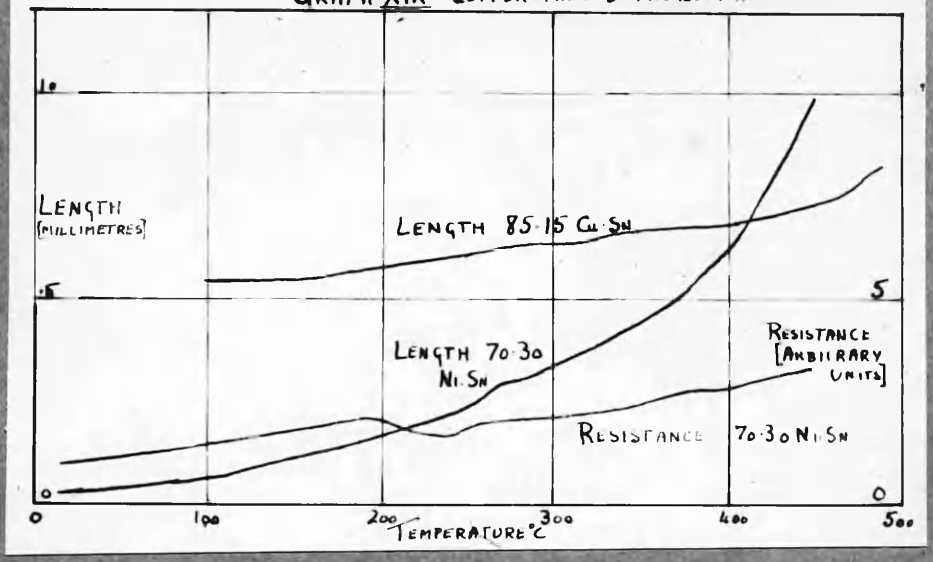
(1) Copper-Cadmium Compacts

Graph XVIII shows dilation curves obtain by heating compacts of varying cadmium content at 2°C. per minute after compacting at 10 tons/sq.in.

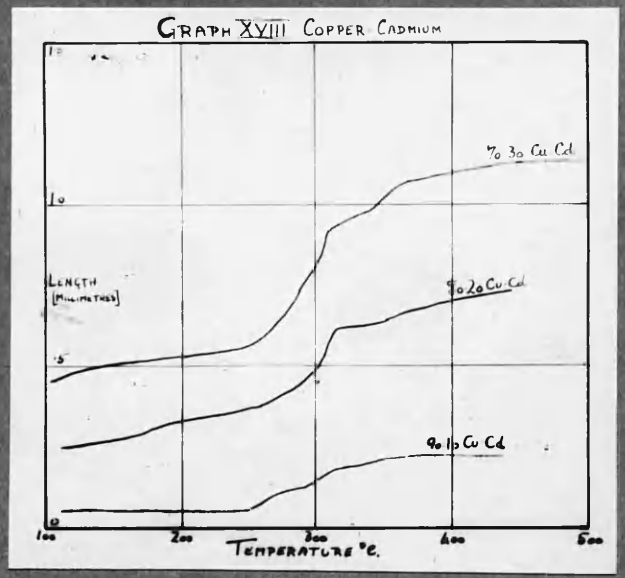
(2) Copper-Tin and Nickel-Tin

Graph XIX shows the dilation curves obtained from 85/15 Copper-Tin and 70/30 Nickel-Tin compacts, and in the case of Nickel-Tin a resistance curve was also obtained. The compacting pressure was 20 tons/sq.in. and the heating rate 2°C./min.

GRAPH XIX COPPER TIN AND NICKEL TIN



GRAPH XVIII COPPER CADMIUM



(3) Nickel-Zinc

Dilation and resistance changes in a 70/30 Nickel-Zinc compact pressed at 20 tons/sq.in. and heated at 2C°/min. are shown in Graph XX.

DISCUSSION

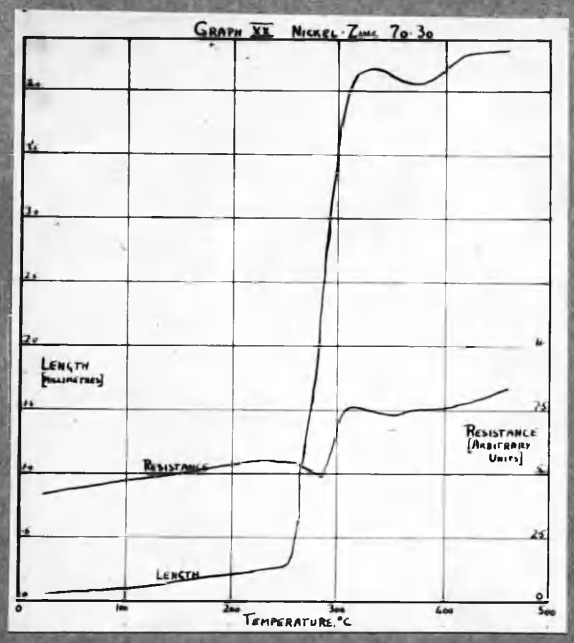
The compacts which contain either zinc or cadmium show the abnormal expansion, whereas in those containing tin the expansion is very slow or absent. A 50/50 copper-nickel compact, pressed at 20 tons/sq.in., also showed an expansion of only 0.11 mm. between 20°C. and 450°C.

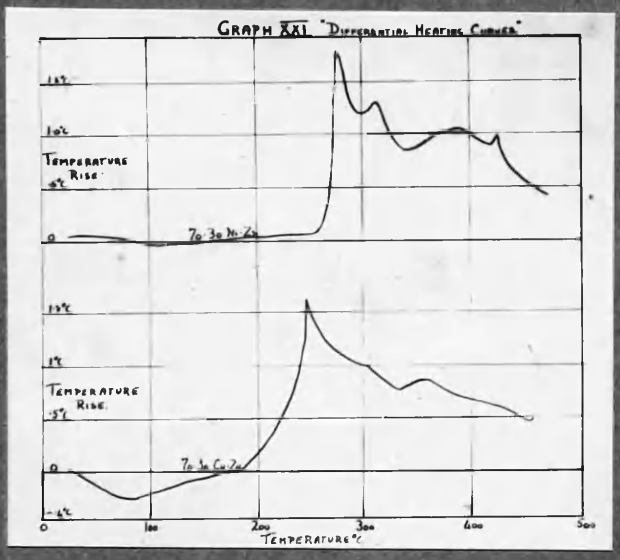
It is believed that the different behaviour of the compacts containing zinc and cadmium is essentially due to the high vapour pressures of these two metals.

The U.S. Bureau of Mines Bulletin 383 lists the temperatures at which certain elements attain a vapour pressure of 0.1 atmosphere. The following values are given for the five elements concerned in this research:-

Cd	Zn	Sn	Cu	Ni
596°C.	817°C.	1978°C.	2435°C.	2594°C.

While these figures do not give an exact quantitative picture of the conditions at about 200°C. they do serve to show the very much higher vapour pressures


Graph XX Nickel-Zinc 70-30
Length [Millimetres]
Resistance [Arbitrary Units]
Resistance
Length
Temperature °C
0
100
200
300
400
500


Graph XXI "Differential Heating Curves"
Temperature Rise
70-30 Ni-Zn
Temperature Rise
70-30 Cu-Zn
Temperature °C
0
100
200
300
400
500

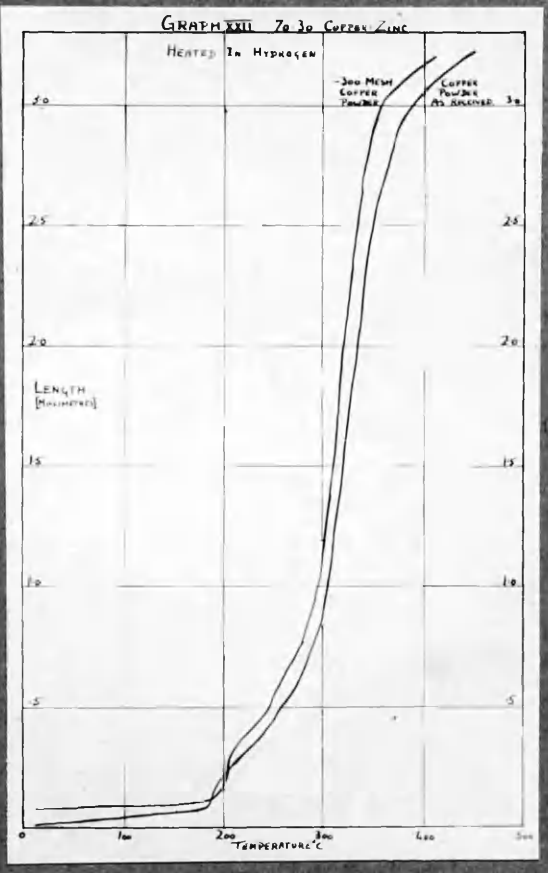
of zinc and cadmium relative to the other three elements.

It is suggested that the rates of transference of tin, copper and nickel are slow because the vapour pressures of these elements are low and such transference as does occur depends on diffusion in the solid state as the controlling factor. On the other hand, with zinc and cadmium the rate of transference is much faster, due to a process of continuous distillation from the free zinc or cadmium on to the surface of the copper or nickel particles.

When nickel-zinc compacts are heated the expansion starts about 30°C. higher than for copper-zinc compacts, but the total expansion and the rate of expansion are both greater. That these differences were not solely due to the fineness of the state of division of the nickel was confirmed by varying the grade of powder used.

ii-d - Effect of Varying the Grade of Powder Used

Two compacts were prepared under identical conditions except that in one the copper powder was used as received and in the other the minus 300 mesh fraction was used. The compacts were pressed at 20 tons/sq.in. and heated in hydrogen at 2C°/min. The dilation curves are shown in Graph XXII.


GRAPH XXII 70 30 COPPER ZINC
HEATED IN HYDROGEN
-300 MESH COPPER POWDER
COPPER POWDER AS RECEIVED
LENGTH (MILLIMETRES)
50
25
20
15
10
5
0
100
200
300
400
500
TEMPERATURE °C

DISCUSSION

With both compacts the temperature at which the abnormal expansion began was very nearly the same and the total abnormal expansion was equal. The coarser powder compact expanded more rapidly in the initial stages but the finer powder compact completed its expansion at a temperature about 30°C. lower.

These differences are small compared with the differences between the nickel-zinc and copper-zinc compacts. It is therefore believed that the difference in behaviour of the nickel-zinc compact is due to some intrinsic property of nickel. Possibly at the lower temperature of 200°C. the activity co-efficient of zinc in solution has a higher value when dissolved in nickel than when dissolved in copper, but when the temperature rises these relative magnitudes are reversed.

On the other hand possibly the adsorbed layer of gas acting as a barrier to the transference is less easily removed from the surface of nickel particles than from the surface of copper particles.

ii-e - Effect of Variation of Furnace Atmosphere

Compacts prepared at 20 tons/sq.in. from 70/30 copper-zinc were made in the standard manner and heated in various atmospheres. Dilation curves were obtained while

heating at a rate of 2°C./min. Table III summarizes the salient features of these curves.

TABLE III

Atmosphere	Beginning of Abnormal Expansion	Rate Between 300°C. and 326°C.
Hydrogen	185°C.	0.04 mm./°C.
Vacuum	210°C.	0.035 mm./°C.
Nitrogen	225°C.	0.01 mm./°C.
Air	235°C.	0.004 mm./°C.

DISCUSSION

The results indicate that the particles have a layer of absorbed gas on the surface which inhibits the beginning of the transfer. This layer is removed more quickly by hydrogen than by heating in a vacuum. This suggests that the layer is oxidizing in nature. The presence of nitrogen or air does not allow the compact to expand normally, so it is probable that these atmospheres either inhibit the removal of the gases from the compact or cause further adsorption of gases.

E - DIFFERENTIAL HEATING CURVES Graph XXI

Differential heating curves for 70/30 nickel-zinc and copper-zinc compacts were obtained while heating in

vacuum at 2°C./minute in the holder earlier described.

DISCUSSION

The initial exothermic heat changes occur at temperatures which nearly coincide with the temperatures of the beginning of the corresponding abnormal expansion. The evolution of heat is more rapid in the case of the nickel compact. This is in keeping with the fact that the rate of expansion is also greater.

The fluctuations in heat evolved above the maximum are probably without fundamental significance. They arise from the heat evolved being quickly conducted to the neutral specimen once a temperature gradient is set up.

F - MICROSTRUCTURE OF PARTIALLY DIFFUSED COMPACTS

Figures 10-17 show the microstructures in the unetched condition of compacts of 70/30 copper-zinc pressed at 20 tons/sq.in. The specimens were prepared by heating them in the vacuum furnace at 2°C./minute and withdrawing them to the cold end of the furnace at 48°C. intervals of temperature from 60°C. to 406°C.

The specimens for microexamination were prepared in the usual manner after breaking them to expose a surface parallel to the direction of the compacting pressure. The

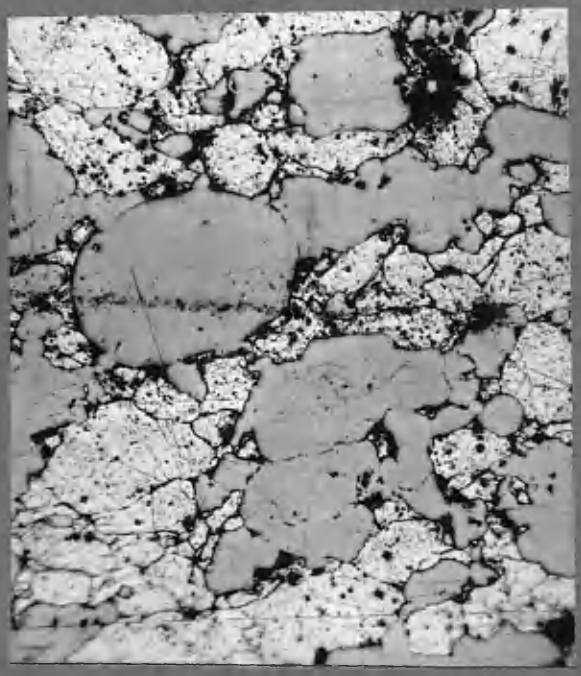


FIGURE 10 HEATED TO 168°C (X700)

FIGURE 11 HEATED TO 216°C (X700)

final polishing was done on a chamois leather pad using first "Brasso" then "Silvo". The specimens were photographed in the unetched condition because the etched structure was complicated unnecessarily by the cold work during pressing. In the etched structure the different phases were less easily observed.

The representation on a photographic plate of the structure observed under the microscope is particularly difficult in the case of this series of specimens because the differences between the phase are differences in tone and colour to which the eye is sensitive. The differences in reflectivity to which the photographic plate is most sensitive are small. By the use of filters it has been possible to heighten the contrast to produce a photograph which is nearer to depicting what is seen by the eye.

Figure 10

This shows the structure obtained after heating to 168°C. The dark areas are copper particles and the light areas zinc. The black areas indicate a small amount of porosity. This porosity is mainly concentrated at copper-zinc interfaces.

The structure is essentially a network of copper particles with the interspaces filled in with the smaller zinc particles.

FIGURE 12 HEATED TO 264°C (X700)

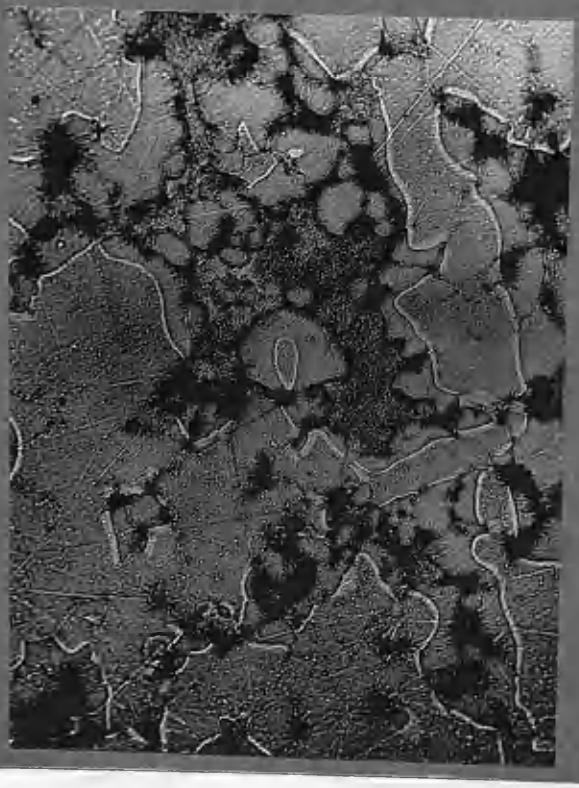


FIGURE 13 HEATED TO 310°C (X350)

Microphotographs taken of specimens which have been heated to temperatures lower than 168°C. are indistinguishable from the structure in figure 10.

Figure 11

This shows the structure obtained when specimens have been heated under similar conditions to 216°C. This is the temperature at which the abnormal expansion is first observed. The difference in tone between figures 10 and 11 is due to the use of a blue filter which was inserted to enable features clearly visible to the eye to be shown on a photographic plate.

It will be seen that at a few points a new phase has appeared at the zinc-copper interface. Under the microscope it is clear that the new phase is situated within the boundary of the original copper grain. The new phase is white in contrast with the red copper and the grey-blue zinc.

Figure 12

This shows the structure after heating to 264°C.

The white phase has increased in amount by extending into the copper particles. The porosity has increased slightly, mainly occurring between the new phase and the zinc. X-ray powder photographs of this specimen and of specimens heated to higher temperatures up to 406°C. showed lines of copper, zinc and beta brass only. The lines

FIGURE 14 HEATED TO 358°C (X1400)

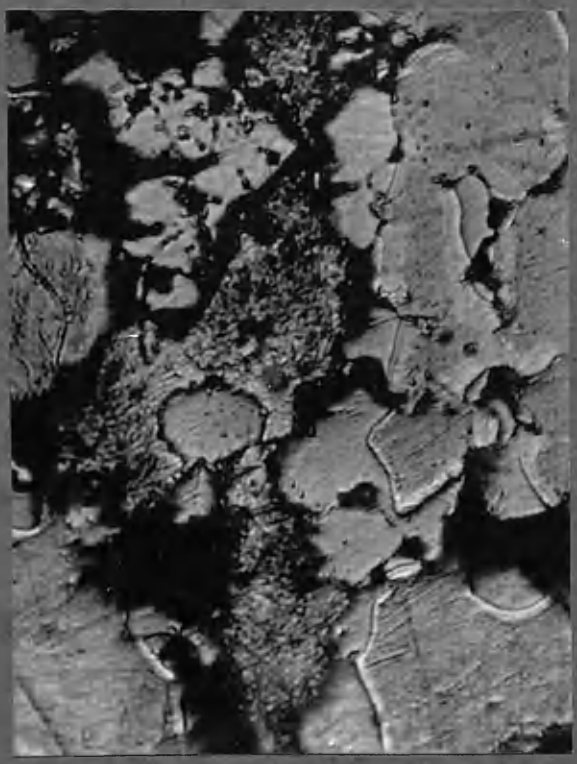


FIGURE 15 HEATED TO 358°C (X700)

observed are reproduced and identified in fig.18. Howat and Craik,[21] using powder specimens in an X-ray apparatus incorporating a goniometer and Geiger counter, have confirmed that the beta phase is the first phase formed when zinc and copper compacts are diffusion treated. It was concluded that this white phase was beta brass.

Figure 13

This shows the structure after heating to 310°C.

A new phase in the form of a light band separating the beta and the unaltered copper is apparent. This appears yellow under the microscope, and, though it could not be confirmed by X-ray analysis because the copper lines were already broadened by cold work, it was assumed to be alpha brass. In the upper centre of the field are mottled areas separated from the beta by areas of porosity. This is the skeleton of zinc which persists at this temperature.

Figures 14 and 15

These show the structure at two different magnifications after heating to 358°C. This is just below the temperature at which the abnormal expansion ceases. The thickness of the alpha band has increased and there is slight evidence of a colour gradient under the microscope. The beta is now the most abundant phase. A small amount of zinc is visible as spots at the extreme top left and the middle of

FIGURE 16 HEATED TO 406°C (X1400)

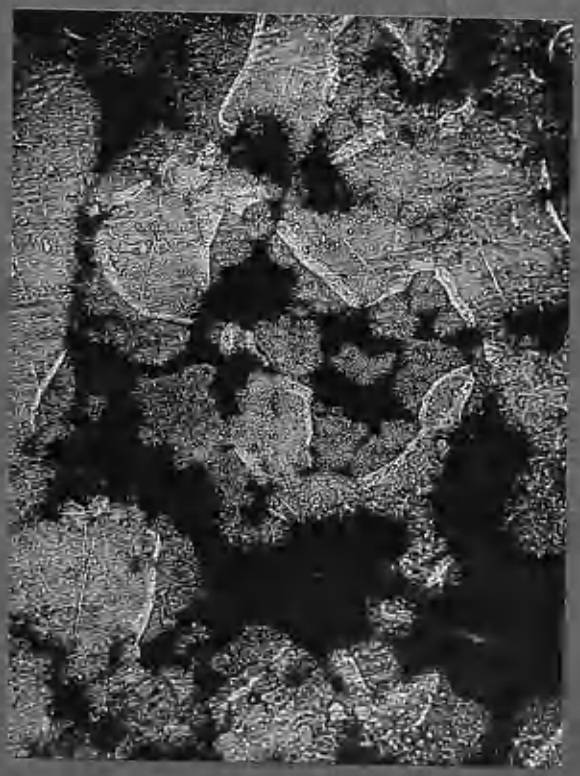


FIGURE 17 HEATED TO 406°C (X350)

the lower edge of figure 14.

Figures 16 and 17

These show the structures at two magnifications at 406°C. - just below the melting point of zinc. Free zinc is no longer visible. It is clear when figures 10 and 17 are compared with one another that the voids in figure 17 occur where the free zinc formerly existed at lower temperatures. The alpha has still further increased in thickness and when examined under the microscope quite clearly shows a colour gradient from yellow next to the beta to orange near the copper. An attempt has been made to show this in figure 16.

DISCUSSION

The photomicrographs show quite clearly that the reason for the expansion is the swelling of the copper grains, most of which are touching one another, by the assimilation of zinc. The first new phase visible under the microscope is beta. It is likely, according to the theory of diffusion, that alpha is in fact formed first but in such small amount that it is not visible. The relative thickness of beta and alpha suggests that the thermodynamic stability of beta is very much greater than alpha. That is, the activity coefficient of zinc in beta brass is lower than in alpha.

FIGURE 18 a LINES FROM COPPER POWDER (Cu)
b LINES FROM UNTREATED 70/30 Cu/Zn COMPACT (Cu & Zn)
c LINES FROM ABOVE COMPACT HEATED TO 264°C (Cu, Zn & β)
d LINES FROM ABOVE COMPACT HEATED TO 406°C (Cu & β)

It is shown in figures 12 to 17 that voidage appears between the beta and the free zinc. This, taken with the evidence in Chapter V, D(ii-c) (page 36 et seq.), confirms that the transference of zinc occurs through the vapour phase.

No phases higher in zinc content than beta are apparent in figures 10 to 17. This is due to the rate of diffusion of zinc being such that the zinc condensed on the beta cannot accumulate in high enough concentration to form gamma in visible amounts.

G - CHANGES IN STRENGTH AFTER HEAT-TREATMENT

Compacts were prepared of 70/30 copper-zinc and 100% copper pressed at 20 tons/sq.in. The compacts were heated at 2°C./minute in the vacuum furnace to various temperatures and withdrawn to the cool end of the furnace. The strength of the cold specimen was determined using the apparatus and method described in Chapter IV. The observations are shown in Tables IV and V.

TABLE IV

COPPER COMPACTS

Heat-Treatment Temperature	Thickness	Load to Fracture
120°C.	0.080"	14.8 lbs.
168°C.	0.079"	16.4 lbs.
216°C.	0.079"	18.1 lbs.
264°C.	0.079"	23.1 lbs.
310°C.	0.079"	28.4 lbs.
358°C.	0.080"	33.6 lbs.
406°C.	0.081"	31.1 lbs.
454°C.	0.081"	39.2 lbs.

TABLE V

70/30 COPPER-ZINC COMPACTS

Diffusion Temperature	Thickness	Load to Fracture
72°C.	0.081"	36.2, 38.2 lbs.
120°C.	0.082"	30.5, 29.1 lbs.
168°C.	0.083"	28.4, 26.3 lbs.
216°C.	0.082"	27.9, 30.7 lbs.
264°C.	0.083"	30.3, 37.1 lbs.
310°C.	0.087"	23.5, 24.0 lbs.
358°C.	0.089"	20.7, 21.6 lbs.
406°C.	0.091"	20.2, 23.9 lbs.

DISCUSSION

The fractures were all of the brittle type; fracture in no case appeared to break the individual particles.

With one exception the results show that the copper compacts progressively increase in strength as the temperature of pretreatment is raised from 120°C. to 454°C. The exception, giving a low value at 406°C., may be due to experimental error. These results, taken in conjunction with the resistivity curve for copper (graph IV), confirm that important changes take place at the interface of copper compacts at low temperatures only slightly above room temperature.

The 70/30 compacts decrease in strength slowly and irregularly until the compact rapidly expands. A sharp drop in strength occurs during the abnormal expansion, and is due probably either to the increase in porosity causing a decrease in effective cross-sectional area, or to the brittleness of the beta formed.

CHAPTER VI

GENERAL DISCUSSION OF RESULTS

As a result of the experiments performed to determine the effect of heat on mixed metal powders, it is suggested that the fundamental process involved in the alloying of certain mixed powders is the mass transfer, through the vapour phase, of the material of higher vapour pressure to the material of lower vapour pressure. In consequence of the diffusion of the volatile metal into the non-volatile metal the particles of the latter swell, so causing the whole compact to expand. That the transfer occurs through the vapour phase is confirmed firstly by the lack of expansion when the volatile metal (either zinc or cadmium) is replaced by tin or nickel, and secondly by examination of the microsections, which show that voids separate the zinc areas from the copper particles.

The thermodynamical possibility of such a process is confirmed by the results of work by Herbena, Siebert and Duffendack.[22] They determined the variation of activity coefficient of zinc in alpha brass containing up to 29% of zinc between 650°C. and 970°C. The coefficients are all less than 0.4 with respect to pure zinc at the same temper-

ature. Extrapolation of their results to 400°C. yields an activity coefficient of about 0.05 in brass containing 29% zinc. This indicates that the vapour pressure of zinc in solution is very much lower than the vapour pressure of pure zinc. Thus the zinc can continuously distil from the free zinc to the copper. The decrease in free energy associated with such a change in activity of zinc in such a process is manifest as part of the heat evolution shown in Graph XXI. The entropy of mixing also contributes to this heat effect.

The changes which occur on heating copper-zinc contacts can most conveniently be considered in three stages.

Stage I - Room Temperature to About 200°C.

Within this range no visible change occurs in the microstructure nor does the overall dimension of the compact alter. The heat change is small or zero within the experimental error. The percentage of soluble zinc remains constant and high.

The changes which do occur seem to be confined to the surface of the particles, such as degassing and increase in contact area by diffusion. The resistivity either falls or does not increase as rapidly as the temperature coefficient of resistance requires.

Since the fracture of all compacts is "intergranular" the variation of strength is due to variation of the bonding between particles. In both pure copper and 70/30 copper-zinc compacts the strength of the compacts changes during this stage, showing that changes occur at the interfaces.

The upper limit of this stage depends on the furnace atmosphere, being lower with an atmosphere of hydrogen or a vacuum, and high with an atmosphere of air or nitrogen. Both the hydrogen atmosphere and the vacuum are conducive to the removal of an adsorbed layer of oxygen or oxide.

All these facts taken together suggest that during Stage I the most important changes taking place are the degassing of the surfaces of the particles, particularly of oxygen, and the increase of the areas of the points of contact.

Stage II - Between 200°C. and 370°C.

During this stage all the zinc is transferred, through the vapour phase, to the copper particles, causing the specimen to dilate. The diffusion of the zinc forms mainly beta, but above 310°C. the amount of alpha becomes appreciable though never as prevalent as either beta or

pure copper. This transference of the zinc causes heat to be evolved and the percentage soluble zinc decreases rapidly.

At the lower temperatures of this stage the resistance continues the downward trend observed in Stage I. This is the result of the same changes at the surface of the particles as in Stage I. At some temperature about the middle of Stage II the resistance either decreases less rapidly or even increases. This is attributed partly to the resistivity of brass being higher than that of copper and zinc, and partly to the increase in resistivity when conducting zinc-copper interfaces disappear and are replaced, when the zinc is transferred, by non-conducting copper-gas interfaces.

During this stage mass transfer of zinc occurs. This is due to the increase in vapour pressure of zinc; the increase in rate of diffusion of zinc in copper; and the removal of the "barrier" of adsorbed gases during Stage I.

Stage III - Above 370°C.

During this stage the amount of alpha brass increases by diffusion of zinc from the beta. The amount of soluble zinc still further decreases. The graph of expansion

is more linear and approximates more closely to the curve for the thermal expansion of brass.

The resistance is changed by two opposing factors, the increase due to alloying and the decrease due to sintering. The tendency to increase being predominant in zinc-rich compacts. (Graphs XV and XVI)

During this stage the beginning of homogenization by diffusion and the early stages of sintering are the main phenomena occurring.

The compacting pressure has a very great effect on the magnitude of the changes occurring during these three stages, but the general features of the stages remain the same. One generalization apparent from the work so far carried out is that Stage II occurs at a lower temperature as the compacting pressure increases. This may indicate that the beginning of the transfer of zinc is by volume diffusion rather than by the vapour phase, since higher compacting pressure would be expected to increase the area of contact, so permitting an appreciable amount of beta formation at a lower temperature. On the other hand higher compacting pressures may rupture "barrier" gas films and so permit continuous distillation of zinc at a lower temperature.

Howat and Craik[21] find that, at temperatures considerably higher than those used in this research, alpha brass is formed at the surface of particles due to loss of zinc by volatilization, so that there arises the intriguing position that a layer of beta brass is sandwiched between two layers of alpha; one arising from the diffusion of zinc from the beta into the central copper core; the other from the diffusion of zinc outwards into space.

CHAPTER VII

CONCLUSION

In this research on the formation of alloy components by powder metallurgical methods from mixed pure metals it has been possible to suggest a process by which certain metal powders begin to approach chemical homogeneity. Much work remains to be done before the full process is clearly understood. It is possible at this stage to suggest the directions in which future work might be profitably undertaken.

The next stage in the approach to equilibrium appears superficially simple, but once each particle is in itself homogeneous how will it become homogeneous with respect to its neighbours? Further research at higher temperatures or longer annealing timesis required to answer this problem.

It has not been possible to explain the effect of compacting pressure on the behaviour of compacts nor has it been possible to vary the grade of powders used over wide ranges. In both these fields much useful information might be revealed by a systematic investigation.

Another field for future work is the effect of

the surface of the particles on the processes occurring. It is felt by the present author that gas films probably play an important part as barriers to both diffusion and sintering. A study of the effect of pretreatment of the powders before mixing would be interesting and enlightening.

As in so many fields of metallurgy full understanding and quantitative treatment of this process of alloying is hampered by the extreme shortage of fundamental data. In this work the lack of diffusion coefficients, activity coefficients and vapour pressures meant that extrapolation, with its associated errors, had to be resorted to. In order to evaluate even these three fundamental and important constants alone a vast amount of research is required.

In conclusion, the author wishes to make certain personal acknowledgments. Owing to circumstances, the experimental work described in this thesis has been carried out partly in the Royal Technical College, Glasgow, and partly at the Victoria University, Manchester. He wishes to thank the Governors of these Institutions for providing

facilities for carrying out the work. The research was suggested by Professor Hay and Dr. D. D. Howat, who gave much encouragement and guidance in the first stages. The author's transfer to Manchester meant a considerable increase in his work due to the reassembly and recalibration of different instruments. The tedium of this work was largely offset by the ready help and interest shown on all occasions by Professor F. C. Thompson.

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APPENDIX A

EXPERIMENTAL OBSERVATIONS

GRAPH 1

Solubility of Zinc after partial diffusion

Solution in 1N HCl for 10 minutes

TREATMENT TEMPERATURE °C	TIME HOURS	% ZINC DISSOLVED
ROOM	4	99.07
250	4	96.87
350	4	84.22
450	4	26.74
550	4	14.68
650	4	13.53
250	4	
350	4	
450	4	7.41 (14.55)*
550	4	
650	4	

* After correction for loss by volatilization

GRAPH 11

Specific volumes of compacts after partial diffusion

Atmosphere- Cracked Ammonia
Treatment time- 4 hours
Composition- 70% Copper 30% Zinc

TREATMENT TEMPERATURE°C	PRESSURE lbs/sq.in.	SPECIFIC VOLUME SINGLE TREATMENT	SPECIFIC VOLUME CUMULATIVE TREATMENT
ROOM	10,000	.178	
	22,400	.159	
250	10,000	.211	.213
	22,400	.168	.175
350	10,000	.249	.270
	22,400	.213	.219
450	10,000	.231	.270
	22,4000	.189	.221
550	10,000	.246	.271
	22,400	.207	.227
650	10,000	.249	.292 (.273)*
	22,400	.220	.244 (.232)*

* Calculated using original weight of sample

GRAPH 111

Specific volumes of compacts after partial diffusion

Atmosphere - Cracked Ammonia
Treatment time - 4 hours
Composition - 100% Cu, 70% Cu, 60% Cu, 100% Zn.
Compacting pressure - 22,400 lbs./sq.in.

Treatment Temperature °C	Specific volume 100%Cu	70%Cu	60%Cu	100%Zn
Room	.147	.152	.150	.158
100	-	.156	.155	-
150	.151	.159	.157	.163
200	-	.159	.176	-
250	-	.169	.194	-
300	.152	.180	.191	.165
350	-	.196	.221	-
400	-	.205	.209	-
450	.152	.206	.221	.165

GRAPH IV COPPER

Resistance and length of pure metal compacts

Column A : Temperature in millivolts on a Chromel-Alumel thermocouple; Cold junction temperature 19.o°C

Column B : Resistance; being the voltage drop in millivolts when a current of 1.o7 Amp is passed.

Column C : Cathetometer reading in millimetres.

A	B	C	A	B	C	A	B	C
.4	15.5	.o95	6.8	lo.1	.194	12.4	4.95	.368
1.4	15.4	.o95	7.o	9.85	.198	12.6	4.8	.374
1.6	15.2	.o94	7.2	9.6	.2o5	12.8	4.65	.378
1.8	15.2	.o97	7.4	9.35	.212	13.o	4.4	.385
2.o	15.1	.o99	7.6	9.1	.218	13.2	4.25	.392
2.2	15.o5	.1o2	7.8	8.9	.224	13.4	4.o	.396
2.4	14.9	.1o6	8.o	8.5	.23o	13.6	3.7	.4oo
2.6	14.6	.1o6	8.2	8.3	.236	13.8	3.4	.4o4
2.8	14.5	.1o9	8.4	8.o	.243	14.o	3.1	.4o8
3.o	14.3	.112	8.6	7.8	.251	14.2	2.8	.413
3.2	14.1	.118	8.8	7.6	.253	14.4	2.55	.418
3.4	14.o	.121	9.o	7.35	.266	14.6	2.25	.425
3.6	13.8	.123	9.2	7.2	.271	14.8	2.o	.428
3.8	13.5	.129	9.4	6.95	.282	15.o	1.8	.431
4.o	13.3	.134	9.6	6.7	.29o	15.2	1.6	.435
4.2	13.15	.138	9.8	6.6	.292	15.4	1.35	.441
4.4	12.8	.142	lo.o	6.45	.296	15.6	1.15	.446
4.6	12.6	.146	lo.2	6.35	.3oo	15.8	.95	.45o
4.8	12.35	.15o	lo.4	6.2	.3o5	16.o	.8o	.453
5.o	12.o5	.157	lo.6	6.1	.311	16.2	.65	.456
5.2	11.8	.162	lo.8	6.o	.323	16.4	.6o	.458
5.4	11.6	.167	11.o	5.85	.33o	16.6	.53	.463
5.6	11.4	.17o	11.2	5.7	.335	16.8	.48	.471
5.8	11.2	.173	11.4	5.5	.339	17.o	.46	.465
6.o	lo.95	.179	11.6	5.4	.35o	17.2	.43	.468
6.2	lo.7	.183	11.8	5.35	.351	17.4	.4o	.47o
6.4	lo.4	.19o	12.o	5.2	.355			
6.6	lo.3	.192	12.2	5.1	.362			

GRAPH 1V ZINC

Resistance and length of pure metal compacts

Cold junction temperature 19.o°C

Resistance current 3.o Amp

A	B	C
.6	2.855	.156
2.2	3.o15	.193
4.o	3.195	.252
4.8	3.235	.275
6.4	3.39o	.328
7.4	3.45o	.369
8.8	3.6o5	.43o
lo.2	3.85o	.482
11.2	4.24o	.513
12oo	4.4o5	.53o
14.4	4.48o	.572
15.o	4.42o	.593
15.4	4.31o	.6oo

GRAPH V

Effect of pressure on tch resistance/temperature and the length/temperature curves

Pressure - 5 tons per sq.in.
Composition - 7o/3o Cu/Zn
Cold junction temperature 24° C
Resistance current - 2.2 Amp

A	B	C	A	B	C	C	A	B	C
.2	13.84	.111	6.4	1o.48		.248	12.4	1.21	2.592
.6	13.91	.113	6.6	9.27		.258	12.6	1.11	2.6o9
.8	14.15	.117	6.8	8.o4		.265	12.8	1.o6	2.612
1.o	14.18	.119	7.o	7.o4		.271	13.o	1.o4	2.617
1.2	14.29	.125	7.2	6.o8		.282	13.2	1.oo	2.625
1.4	14.4o	.127	7.4	5.11		.285	13.4	.98	2.627
1.6	14.6o	.13o	7.6	4.39		.295	13.6	.97	2.635
1.8	14.79	.135	7.8	3.78		.3o2	13.8	.96	2.636
2.o	14.91	.137	8.o	3.27		.32o	14.o	.96	2.642
2.2	15.14	.142	8.2	2.86		.341	14.2	.97	2.647
2.4	15.24	.148	8.4	2.62		.353	14.4	.97	2.649
2.6	15.44	.151	8.6	2.39		.384	14.6	.97	2.657
2.8	15.67	.156	8.8	2.27		.411	14.8	.98	2.668
3.o	15.81	.16o	9.o	2.24		.438	15.o	.97	2.67o
3.2	15.88	.163	9.2	2.23		.481	15.2	.98	2.674
3.4	15.9o	.167	9.4	2.27		.519	15.4	.97	2.684
3.6	15.87	.174	9.6	2.35		.572	15.6	.975	2.694
3.8	15.87	.18o	9.8	2.38		.627	15.8	.975	2.7o1
4.o	15.77	.186	1o.o	2.4o		.691	16.o	.97	2.715
4.2	15.62	.189	1o.2	2.37		.769	16.2	.975	2.721
4.4	15.57	.192	1o.4	2.27		.859	16.4	.98	2.738
4.6	15.45	.195	1o.6	2.19		.973	16.6	.99	2.751
4.8	15.18	.2o1	1o.8	1.91	1	.o85	16.8	1.o2	2.752
5.o	14.98	.2o6	11.o	1.76	1	.272	17.o	1.o4	2.762
5.2	14.64	.214	11.2	1.66	1	.61o	17.2	1.o6	2.77o
5.4	14.26	.216	11.4	1.64	1	.872	17.4	1.o7	2.769
5.6	13.85	.222	11.6	1.63	2	.11o	17.6	1.o9	-
5.8	13.26	.232	11.8	1.6o	2	.3o1	17.8	1.11	-
6.o	12.5	.24o	12.o	1.48	2	.431	18.o	1.14	-
6.2	11.45	.242	12.2	1.32	2	.548			

GRAPH VL (effect of pressure)

Pressure - 1o tons per sq. in.

Composition - 7o/3o Cu/Zn

Cold junction temperature - 23.5°C

Resistance current - 3 amp

A	B	C	A	B	C	A	B	C
.4	13.58	.o17	6.4	13.39	.151	12.4	7.2o	2.371
.6	13.69	.o19	6.6	12.48	.155	1266	6.96	2.469
.8	113.82	.o22	6.8	11.73	.157	12.8	6.66	2.545
1.o	13.91	.o24	7.o	1o.87	.166	13.o	6.36	2,559
1.2	13.97	.o31	7.2	1o.12	.172	13.2	6.17	2.565
1.4	14.o9	.o37	7.4	9.48	.179	13.4	6.oo	2.576
1.6	14.12	.o4o	7.6	8.98	.185	13.6	5.85	2.58o
1.8	14.29	.o42	7.8	8.45	.19o	13.8	5.75	2.588
2.o	14.36	.o46	8.o	8.o1	.2o5	14.o	5.71	2.593
2.2	14.5o	.o51	8.2	7.79	.215	14.2	5.74	2.596
2.4	14.57	.o53	8.4	7.53	.233	14.4	5.78	2.6o1
2.6	14.69	.o57	8.6	7.36	.252	14.6	5.78	2.6o7
2.8	14.81	.o62	8.8	7.28	.273	14.8	5.76	2.611
3.o	14.95	.o66	9.o	7.2o	.296	15.o	5.79	2.622
3.2	15.1o	.o72	9.2	7.23	.331	15.2	5.85	2.635
3.4	15.17	.o78	9.4	7.29	.365	15.4	5.7o	2.643
3.6	15.35	.o8o	9.6	7.38	.421	15.6	5.57	2.653
3.8	15.26	.o82	9.8	7.67	.464	15.8	5.59	2.67o
4.o	15.23	.o88	1o.o	7.87	.5o8	16.o	5.57	2.685
4.2	15.2o	.o92	1o.2	8.o5	.628	16.2	5.58	2.653
4.4	15.17	.o95	1o.4	8.23	.7oo	16.4	5.62	2.664
4.6	15.13	.1o2	1o.6	8.25	.8o1	16.6	5.62	2.672
4.8	15.12	.1o8	1o.8	8.o4	.965	16.8	5.59	2.69o
5.o	15.o1	.114	11.o	7.86	1.115	17.o	5.66	2.7o4
5.2	14.89	.118	11.2	7.6o	1.273	17.2	5.66	2.718
5.4	14.82	.125	11.4	7.55	1.463	17.4	5.69	2.732
5.6	14.82	.13o	11.6	7.5o	1.653	17.6	5.76	2.75o
5.8	14.54	.136	11.8	7.45	1.843	17.8	5.78	2.762
6.o	14.35	.141	12.o	7.39	2.o34	18.o	5.84	2.777
6.2	14.9o	.147	12.2	7.33	2.295			

GRAPH V11 (Effect of pressure)

Graph X111 (Effect of Composition)

Pressure 2o tons per sq. in.

Composition 7o/3o Cu/Zn

Cold junction termperature 22.5°C

Resistance current 1.o amp.

A	B	C	A	B	C	A	B	C
.4	4.155	.o74	7.o	4.12	.235	13.o	4.6oo	1.913
.6	4.175	.o75	7.2	3.98	.238	13.2	4.36o	1.945
.8	4.245	.o75	7.4	3.86	.247	13.4	4.o5o	1.958
1.6	4.35o	.o9o	7.6	3.75	.254	13.6	3.79	1.971
1.8	4.37o	.o95	7.8	3.56	.261	13.8	3.41	1.915
2.o	4.38o	.1o3	8.o	3.46	.268	14.o	3.oo	1.989
2.2	4.42o	.121	8.2	3.39	.281	14.2	2.71	1.995
2.4	4.445	.121	8.4	3.31	.287	14.4	2.38	2.oo2
2.6	4.445	.125	8.6	3.27	.291	14.6	2.17	2.oo5
2.8	4.445	.132	8.8	3.25	.3o4	14.8	2.o5	2.o1o
3.o	4.485	.137	9.o	3.275	.322	15.o	1.92	2.o12
3.2	4.495	.142	9.2	3.335	.341	15.2	1.83	2.o2o
3.4	4.52o	.147	9.4	3.445	.372	15.4	1.74	2.o4o
3.6	4.525	.154	9.6	3.63o	.412	15.6	1.67	2.o49
3.8	4.535	.162	9.8	3.79o	.467	15.8	1.63	2.o55
4.o	4.56o	.166	1o.o	3.95o	.691	16.o	1.57	2.o64
4.2	4.565	.17o	1o.2	4.165	.811	16.2	1.55	2.o85
4.4	4.57o	.177	1o.4	4.355	.982	16.4	1.52	2.141
4.6	4.555	.182	1o.6	4.49o	1.123	16.6	1.48	2.168
4.8	4.555	.189	1o.8	4.63o	1.249	16.8	1.46	2.192
5.o	4.555	.192	11.o	4.79o	1.345	17.o	1.45	2.21o
5.2	4.555	.198	11.2	4.935	1.417	17.2	1.44	2.223
5.4	4.555	.2o4	11.4	5.14o	1.522	17.4	1.43	2.232
5.6	4.555	.2o5	11.6	5.25o	1.598	17.6	1.42	2.245
5.8	4.555	.21o	11.8	5.3oo	1.667	17.8	1.41	2.27o
6.o	4.51o	.21o	12.o	5.29o	1.723	18.o	1.4o	2.295
6.2	4.48o	.216	12.2	5.235	1.78o			
6.4	4.41o	.222	12.4	5.16o	1.827			
6.6	4.36o	.231	12.6	5.o2o	1.859			
6.8	4.25	.235	12.8	4.81o	1.887			

GRAPH V111 (Effect of pressure)

Pressure - 3o tons per sq. in.

Composition - 7o/3o Cu/Zn

Cold junction temperature - 2o.5°C

Resistance current - o.5 amp.

A	B	C	A	B	C	A	B	C
.o	-	.o1	7.4	1.81o	.19	12.4	1.o65	1.22
.8	-	.o2	7.6	1.77o	.2o	12.6	1.o52	1.26
2.7	-	.o6	7.8	1.68o	.2o	12.8	1.o41	1.3o
3.o	2.o65	-	8.o	1.635	.21	13.o	1.o35	1.33
3.2	-	.o7	8.2	1.565	.22	13.2	1.o24	1.36
3.4	2.o58	.o8	8.4	1.51o	.22	13.4	1.o15	1.39
3.6	-	.o8	8.6	1.455	.23	13.6	1.oo6	1.43
3.8	2.o4o	-	8.8	1.41o	.25	13.8	1.oo3	1.46
4.o	-	.o9	9.o	1.365	.27	14.o	1.oo1	1.5o
4.2	2.o22	-	9.2	1.327	.29	14.2	1.oo1	1.55
4.4	-	.1o	9.4	1.295	.31	14.4	1.ooo	1.57
4.6	2.o5o	-	9.6	1.265	.35	14.6	1.ooo	1.6o
4.8	-	.1o	9.8	1.255	.41	14.8	.995	1.62
5.o	2.o38	-	1o.o	1.245	.47	15.o	.99o	1.63
5.2	-	.11	1o.2	1.232	.53	15.2	.981	1.64
5.4	2.o32	-	1o.4	1.221	.59	15.4	.975	1.65
5.6	-	.12	1o.6	1.2o5	.67	15.6	.971	1.66
5.8	2.o25	-	1o.8	1.188	.76	15.8	.955	1.67
6.o	-	.14	11.o	1.17o	.82	16.o	.941	1.69
6.2	2.o65	.15	11.2	1.149	.9o	16.2	.925	1.69
6.4	-	.16	11.4	1.131	.96	16.4	-	1.7o
6.6	2.o41	.17	11.6	1.119	1.o3	16.6	.89o	1.71
6.8	2.ooo	.18	11.8	1.1o5	1.o8	16.8	.878	1.73
7.o	1.95o	.18	12.o	1.o91	1.14	17.o	.868	1.75
7.2	1.9o5	.19	12.2	1.o75	1.18			

GRAPH 1X (Effect of pressure)

Pressure - 5o tons per sq. in.

Composition - 7o/3o Cu/Zn

Cold junction temperature - 2o.5°C

Resistance current

A	B	C	A	B	C	A	B	C
.2	1.755	.91	6.6	1.696	1.o6	12.4	1.o59	2.21
.4	1.75o	.92	6.8	1.683	1.o6	12.6	1.o53	2.24
.6	1.752	.92	7.o	1.658	1.o6	12.8	1.o44	2.27
.8	1.749	.93	7.2	-	-	13.o	1.o34	2.31
1.o	1.746	.93	7.4	1.622	1.o8	13.2	1.o24	2.33
1.8	1.746	.95	7.6	1.596	1.o8	13.4	1.o15	2.36
2.o	1.75o	.96	7.8	1.558	1.o9	13.6	1.oo8	2.41
2.2	1.752	.96	8.o	1.522	1.1o	13.8	1.oo1	2.43
2.4	1.751	.97	8.2	1.485	1.1o	14.o	.996	2.46
2.6	1.752	.97	8.4	1.452	1.12	14.2	.993	2.5o
2.8	1.751	.98	8.6	1.42o	1.15	14.4	.989	2.52
3.o	1.75o	.98	8.8	1.389	1.18	14.6	.983	2.57
3.2	1.748	.98	9.o	1.364	1.22	14.8	.978	2.59
3.4	1.751	.99	9.2	1.333	1.25	15.o	.972	2.6o
3.6	1.749	.99	9.4	1.3o8	1.3o	15.2	-	-
3.8	1.748	.99	9.6	1.286	1.36	15.4	.958	2.63
4.o	1.746	.99	9.8	1.274	1.41	15.6	.95o	2.64
4.2	1.744	1.oo	1o.o	1.253	1.48	15.8	.943	2.65
4.4	1.744	1.o1	1o.2	1.229	1.55	16.o	.934	2.66
4.6	1.746	1.o1	1o.4	1.2o8	1.62	16.2	.924	2.68
4.8	1.743	1.o1	1o.6	1.178	1.69	16.4	.9o7	2.69
5.o	1.74o	1.o2	1o.8	1.153	1.76	16.6	.9o1	2.7o
5.2	1.741	1.o1	11.o	1.136	1.83	16.8	.899	2.72
5.4	1.738	1.o1	11.2	1.125	1.91	17.o	.895	2.74
5.6	1.732	1.o2	11.4	1.111	1.99	17.2	.893	2.75
5.8	1.73o	1.o3	11.6	1.1o3	2.o4	17.4	.894	2.76
6.o	1.722	1.o3	11.8	1.o96	2.o9	17.6	.893	2.78
6.2	1.719	1.o4	12.o	1.o8o	2.15	17.8	.896	2.79
6.4	1.7o8	1.o5	12.2	1.o7o	2.19	18.o	.899	2.8o

(o.9 should be subtracted from each reading in column C in order to obtain the points on the graph)

GRAPH X (Effect of pressure)

Pressure - 7o tons per sq. in.

Composition - 7o/3o Cu/Zn

Cold junction temperature - 23.o° C

Resistance current - o.5 amp.

A	B	C
.2	19.61	.o3
.6	19.35	.o4
.8	19.13	.o4
1.o	19.1o	.o5
1.2	19.o8	.o5
1.4	18.9o	.o5
1.6	18.86	.o55
1.8	18.91	.o6
2.o	18.73	.o65
2.2	18.78	.o68
2.4	18.68	.o72
2.6	18.55	.o75
2.8	18.45	.o82
3.o	18.4o	.o9o
3.2	18.28	.o95
3.4	17.95	.o95
3.6	17.88	.1oo
3.8	17.94	.1o5
4.o	17.7o	.1o5
4.2	17.75	.11o
4.4	17.67	.115
4.6	17.63	.115
4.8	17.45	.121
5.o	17.25	.126
5.2	17.o2	.132
5.4	16.8o	.135
5.6	16.68	.144
5.8	16.45	.145
6.o	16.35	.147
6.2	16.24	.152
6.4	16.15	.155
6.6	15.94	.157
6.8	15.62	.164
7.o	15.55	.17o
7.2	15.32	.175
7.4	15.1o	.183
7.6	14.78	.192
7.8	14.38	.199
8.o	14.1o	.217
8.2	13.75	.235
8.4	13.4o	.255
8.6	13.21	.291
8.8	12.75	.328
9.o	12.38	.375
9.2	12.1o	.424
9.4	11.73	.483
9.6	11.36	.546
9.8	1o.84	.633
1o.o	1o.41	.7o5
1o.2	1o.o8	.783
1o.4	9.68	.86o
1o.6	9.o4	.955
1o.8	8867	1.o58
11.o	8.24	1.135
11.2	7.94	1.211
11.4	7.86	1.289
11.6	7.61	1.355
11.8	7.51	1.422
12.o	7.4o	1.48o
12.2	7.28	1.533
12.4	7.23	1.573
12.6	6.98	1.621
12.8	6.89	1.644
13.o	6.72	1.665
13.2	6.63	1.686
13.4	6.51	1.716
13.6	6.43	1.746
13.8	6.38	1.775
14.o	6.3o	1.795
14.2	6.2o	1.818
14.4	6.11	1.834
14.6	5.98	1.853
14.8	5.82	1.879
15.o	5.76	1.895
15.2	5.61	1.9oo
15.4	5.54	1.9o2
15.6	5.39	1.9o6
15.8	5.27	1.912
16.o	5.19	1.917
16.2	5.14	1.923
16.4	5.o9	1.929
16.6	5.o6	1.942
16.8	5.o2	1.957
17.o	4.98	1.969
17.2	4.97	1.988
17.4	4.98	2.oo5
17.6	4.99	2.o18
17.8	5.oo	2.o48
18.o	4.99	2.o75
18.6	4.99	2.128
19.4	5.oo	2.2o5

GRAPH X1 (Effect of composition)

Pressure - 20 tons per sq. in.

Composition - 90/10 Cu/Zn

Cold junction temperature - 21.5°C

Resistance current - 3 amp

A	B	C	A	B	C	A	B	C
.2	11.48	.053	6.0	10.50	.155	11.6	2.66	.631
.4	11.55	.057	6.2	10.20	.163	11.8	2.64	.645
.6	11.59	.056	6.4	9.80	.165	12.0	2.62	.671
1.0	11.63	.058	6.6	9.50	.173	12.2	2.58	.682
1.2	11.68	.061	6.8	9.00	.179	12.4	2.51	.703
1.4	11.75	.064	7.0	8.40	.186	12.6	2.42	.723
1.6	11.80	.066	7.2	7.50	.192	12.8	2.36	.725
1.8	11.85	.073	7.4	6.75	.203	13.0	2.28	.745
2.0	11.80	.076	7.6	6.10	.202	13.2	2.21	.755
2.2	11.95	.082	7.8	5.50	.210	13.4	2.15	.765
2.4	12.00	.089	8.0	5.05	.213	13.6	2.07	.777
2.6	12.05	.092	8.2	4.55	.222	13.8	2.00	.773
2.8	12.15	.096	8.4	4.10	.231	14.0	1.94	.775
3.0	12.15	.098	8.6	3.75	.231	14.2	1.89	.789
3.2	12.20	.103	8.8	3.55	.246	14.4	1.83	.785
3.4	12.15	.101	9.0	3.30	.263	14.6	1.77	.792
3.6	12.15	.102	9.2	3.15	.280	14.8	1.71	.800
3.8	12.05	.104	9.4	3.05	.292	15.0	1.66	.801
4.0	11.90	.112	9.6	2.90	.306	15.2	1.61	.811
4.2	11.80	.114	9.8	2.83	.280	15.4	1.57	.827
4.4	11.80	.121	10.0	2.79	.348	15.6	1.54	.831
4.6	11.70	.127	10.2	2.79	.381	15.8	1.51	.840
4.8	11.55	.130	10.4	2.84	.421	16.0	1.50	.848
5.0	11.40	.135	10.6	2.85	.466	16.2	1.48	.859
5.2	11.30	.143	10.8	2.86	.497	16.4	1.47	.865
5.4	11.15	.143	11.0	2.83	.532	16.6	1.46	.870
5.6	10.90	.152	11.2	2.79	.575	16.8	1.45	.883
5.8	10.70	.152	11.4	2.74	.602	17.0	1.44	.890

Graph XII (Effect of composition)

Pressure - 20 tons per sq. in.

Composition - 80/20 Cu/Zn

Cold junction temperature - 23.0°C

Resistance current - 0.5 amp

A	B	C	A	B	C	A	B	C
.2	5.26	.081	7.4	.203	3.95	13.0	2.54	1.470
.8	5.29	.085	7.6	.231	3.75	13.2	2.51	1.480
1.2	5.38	.095	7.8	.235	3.51	13.4	2.46	1.490
1.6	5.46	.095	8.0	.245	3.32	13.6	2.41	1.508
2.0	5.48	.102	8.2	.250	3.20	13.8	2.37	1.510
2.4	5.52	.113	8.4	.262	3.08	14.0	2.30	1.510
2.8	5.58	.118	8.6	.273	2.94	14.2	2.25	1.510
3.2	5.63	.120	8.8	.292	2.84	14.4	2.17	1.513
3.4	5.65	.125	9.0	.312	2.75	14.6	2.10	1.516
3.6	5.65	.130	9.2	.331	2.70	14.8	2.03	1.518
3.8	5.61	.138	9.4	.372	2.64	15.0	1.96	1.525
4.0	5.60	.140	9.6	.422	2.60	15.2	1.90	1.532
4.2	5.58	.143	9.8	.480	2.57	15.4	1.82	1.548
4.4	5.60	.145	10.0	.550	2.55	15.6	1.75	1.555
4.6	5.60	.152	10.2	.685	2.522	15.8	1.67	1.565
4.8	5.54	.152	10.4	.808	2.40	16.0	1.61	1.590
5.0	5.53	.165	10.6	.872	2.50	16.2	1.56	1.608
5.2	5.50	.170	10.8	.928	2.515	16.4	1.51	1.622
5.4	5.41	.178	11.0	.998	2.520	16.6	1.47	1.648
5.6	5.35	.178	11.2	1.047	2.525	16.8	1.44	1.662
5.8	5.29	.178	11.4	1.110	2.520	17.0	1.41	1.675
6.0	5.21	.181	11.6	1.170	2.535	17.2	1.38	1.692
6.2	5.12	.189	11.8	1.211	2.525	17.4	1.36	1.715
6.4	5.00	.190	12.0	1.250	2.540	17.6	1.33	1.740
6.6	4.85	.201	12.2	1.302	2.57	17.8	1.31	1.752
6.8	4.66	.210	12.4	1.320	2.60	18.0	-	1.756
7.0	4.44	.215	12.6	1.395	2.58			1.98
7.2	4.23	.220	12.8	1.435	2.57	20.5	1.29	1.985

GRAPH XlV (Effect of composition)

Pressure - 2o tons per sq. in.

Composition - 6o/4o Cu/Zn

Cold junction temperature - 22.o°C

Resistance current - 1.o amp.

A	B	C	A	B	C	A	B	C
.2	3.43	.o21	6.2	3.73	.14o	12.2	2.62	2.185
.4	3.45	.o22	6.4	3.69	.143	12.4	2.52	2.285
.6	3.47	.o22	6.6	3.66	.153	12.6	2.43	2.386
.8	3.5o	.o22	6.8	3.59	.166	12.8	2.32	2.489
1.o	3.51	.o24	7.o	3.51	.172	13.o	2.24	2.58o
1.2	3.52	.o24	7.2	3.44	.174	13.2	2.19	2.667
1.4	3.54	.o26	7.4	3.38	.18o	13.4	2.15	2.721
1.6	3.56	.o3o	7.6	3.28	.192	13.6	2.11	2.742
1.8	3.58	.o33	7.8	3.17	.196	13.8	2.03	2.769
2.o	3.59	.o38	8.o	3.o6	.2o3	14.o	1.97	2.795
2.2	3.6o	.o43	8.2	2.93	.212	14.2	1.83	2.8o9
2.4	3.62	.o49	8.4	2.81	.222	14.4	1.68	2.816
2.6	3.64	.o51	8.6	2.76	.23o	14.6	1.57	2.83o
2.8	3.65	.o57	8.8	2.72	.252	14.8	1.48	2.832
3.o	3.65	.o59	9.o	2.7o	.281	15.o	1.41	2.845
3.2	3.67	.o64	9.2	2.71	.328	15.2	1.39	2.855
3.4	3.66	.o68	9.4	2.75	.378	15.4	1.37	2.85o
3.6	3.69	.o75	9.6	-	.451	15.6	1.33	2.856
3.8	3.7o	.o78	9.8	2.81	.562	15.8	1.28	2.865
4.o	3.71	.o84	1o.o	2.9o	.713	16.o	1.25	2.883
4.2	3.72	.o86	1o.2	2.96	.852	16.2	1.22	2.9o2
4.4	3.74	.o91	1o.4	3.o2	.982	16.4	1.19	2.911
4.6	3.74	.o97	1o.6	3.o6	1.132	16.6	1.17	2.924
4.8	3.73	.1o1	1o.8	3.o2	1.243	16.8	1.16	2.939
5.o	3.72	.1o9	11.o	2.96	1.41o	17.o	1.15	2.968
5.2	3.73	.112	11.2	2.93	1.529	17.2	1.14	2.991
5.4	3.73	.118	11.4	2.88	1.673	17.4	1.13	3.o12
5.6	3.73	.122	11.6	2.88	1.788	17.6	1.125	3.o45
5.8	3.74	.129	11.8	2.87	1.913	17.8	1.12	3.o6o
6.o	3.74	.134	12.o	2.75	2.o85			

GRAPH XV (Effect of Composition)

Pressure - 2o tons per sq. in.

Composition - 5o/5o Cu/Zn

Cold junction temperature - 21.5°C

Resistance current - 3.o amp

A	B	C
.2	4.815	.o68
1.2	4.96o	.o74
1.4	4.95o	.o78
1.6	5.o7	.o88
1.8	5.11	.o89
2.o	5.15	.o95
2.2	5.18	.o97
2.4	5.23	.1oo
2.6	5.27	.1o7
2.8	5.32	.112
3.o	5.34	.118
3.2	5.37	.125
3.4	5.4o	.128
3.6	5.45	.132
3.8	5.48	.139
4.o	5.53	.142
4.2	5.56	.148
4.4	5.63	.153
4.6	5.64	.16o
4.8	5.65	.165
5.o	5.66	.171
5.2	5.7o	.172
5.4	5.71	.178
5.6	5.71	.184
5.8	5.74	.189
6.o	5.72	.195
6.2	5.69	.2o2
6.4	5.67	1206
6.6	5.61	.223

A	B	C
6.8	5.46	.233
7.o	5.33	.235
7.2	5.13	.24o
7.4	4.97	.247
7.6	4.83	.255
7.8	4.72	.261
8.o	4.54	.269
8.2	4.47	.292
8.4	4.41	.3o9
8.6	4.38	.329
8.8	4.35	.361
9.o	4.34	.416
9.2	4.34	.453
9.4	4.37	.531
9.6	4.41	.663
9.8	4.45	.769
1o.o	4.5o	.892
1o.2	4.52	1.o69
1o.4	4.57	1.27o
1o.6	4.54	1.431
o.8	4.49	1.557
11.o	4.45	1.749
11.2	4.47	1.911
11.4	4.5o	2.13o
11.6	4.53	2.341
11.8	4.55	2.481
12.o	4.58	2.628
12.2	4.64	2.812
12.4	4.66	2.951
12.6		

A	B	C
12.6	4.74	3.138
12.8	4.77	3.241
13.o	4.85	3.373
13.2	4.87	3.473
13.4	4.92	3.553
13.6	5.o2	3.6o5
13.8	5.1o	3.659
14.o	5.15	3.684
14.2	5.19	3.699
14.4	5.25	3.718
14.6	5.3o	3.735
14.8	5.35	3.761
15.o	5.39	3.772
15.2	5.41	3.783
15.4	5.42	3.8o2
15.6	5.43	3.817
15.8	5.46	3.827
16.o	5.53	3.841
16.2	5.58	3.859
16.4	5.61	3.876
16.6	5.67	3.898
16.8	5.7o	3.935
17.o	5.74	3.969
17.2	5.76	3.972
17.4	5.78	3.981
17.6	5.8o	4.011
17.8	5.8o	4.o31
18.o	5.8o	4.o52

GRAPH XVI (Effect of composition)

Pressure - 20 tons per sq, in.

Composition - 40/60 Cu/Zn

Cold junction temperature - 21.0°C

Resistance current - 3.0 amp.

A	B	C	A	B	C	A	B	C
.2	4.40	.068	6.6	5.21	.211	12.2	14.10	2.525
1.2	4.57	.083	6.8	5.20	.218	12.4	4.12	2.702
1.4	4.60	.092	7.0	5.19	.223	12.6	4.13	2.941
1.6	4.62	.092	7.2	5.14	.225	12.8	4.19	3.189
1.8	4.63	.096	7.4	5.12	.232	13.0	4.21	3.392
2.0	4.65	.107	7.6	5.04	.239	13.2	4.22	3.587
2.2	4.67	.109	7.8	4.93	.246	13.4	4.32	3.777
2.4	4.69	.111	8.0	4.88	.250	13.6	4.38	3.965
2.6	4.72	.119	8.2	4.75	.262	13.8	4.47	4.151
2.8	4.75	.122	8.4	4.64	.265	14.0	4.60	4.281
3.0	4.77	.125	8.6	4.49	.284	14.2	4.69	4.395
3.2	4.78	.129	8.8	4.40	.303	14.4	4.80	4.468
3.4	4.80	.132	9.0	4.33	.321	14.6	4.86	4.533
3.6	4.88	.135	9.2	4.29	.351	14.8	4.98	4.622
3.8	4.92	.141	9.4	4.27	.391	15.0	5.10	4.679
4.0	4.94	.149	9.6	4.25	.448	15.2	5.25	4.727
4.2	4.94	.153	9.8	4.24	.515	15.4	5.48	4.768
4.4	4.98	.160	10.0	4.26	.622	15.6	5.68	4.795
4.6	5.06	.163	10.2	4.28	.730	15.8	5.87	4.814
4.8	5.03	.166	10.4	4.31	.900	16.0	6.07	4.843
5.0	5.11	.169	10.6	4.35	1.083	16.2	6.30	4.859
5.2	5.12	.172	10.8	4.42	1.248	16.4	6.46	4.879
5.4	5.15	.179	11.0	4.39	1.356	16.6	6.58	4.895
5.6	5.19	.184	11.2	4.36	1.564	16.8	6.74	4.911
5.8	5.23	.194	11.4	4.30	1.712	17.0	6.90	4.976
6.0	5.24	.198	11.6	4.24	1.858	17.2	7.04	4.985
6.2	5.21	.203	11.8	4.16	2.072	17.4	7.17	5.022
6.4	5.20	.206	12.0	4.44	2.251	17.6	7.31	5.015
						17.8	7.45	5.030

GRAPH XVIII (Copper - Cadmium)

Pressure - 2o tons

Composition - A 7o/3o; B 8o/2o; C 9o/1o; Cu/Cd

Cold junction temperature - 17°C

mv	A	B	C
o.o	.41	.28	.o5
3.o	.49	.33	.o4
3.2	.49	.33	.o4
3.4	.52	.33	.o5
3.6	.55	.34	.o5
3.8	.56	.33	.o4
4.o	.57	.34	.o3
4.2	.58	.34	.o6
4.4	.57	.34	.o3
4.6	.59	.35	.1o
4.8	.59	.36	.o7
5.o	.6o	.37	.o5
5.2	.61	.37	.o5
5.4	.61	.36	.o5
5.6	.61	.37	.o4
5.8	.61	.37	.o6
6.o	.62	.38	.o5
6.2	.61	.38	.o7
6.4	.61	.39	.o5
6.6	.61	.39	.o4
6.8	.61	.41	.o5
7.o	.61	.41	.o4
7.2	.61	.41	.o6
7.4	.62	.43	.o6
7.6	.61	.43	.o6
7.8	.61	.42	.o5
8.o	.62	.43	.o5
8.2	.63	.44	.o6
8.4	.63	.44	.o5
8.6	.64	.45	.o6
8.8	.65	.44	.o5
9.o	.65	.45	.o6
9.2	.66	.45	.o5
9.4	.66	.46	.o5
9.6	.66	.46	.o5
9.8	.67	.47	.o6
1o.o	.68	.47	.o6
1o.2	.69	.48	.o7
1o.4	.73	.49	.o9
1o.6	.74	.5o	.11
1o.8	.77	.51	.11
11.o	.79	.54	.11
11.2	.82	.55	.12
11.4	.85	.57	.12
11.6	.87	.59	.14
11.8	.91	.61	.15
12.o	.98	.62	.16
12.2	1.o2	.68	.18
12.4	1.o3	.71	.18
12.6	1.o5	.71	.19
12.8	1.o5	.71	.19
13.o	1.o7	.73	.19
13.2	1.o7	.72	.2o
13.4	1.o8	.73	.2o
13.6	1.o8	.72	.21
13.8	1.12	.72	.21
14.o	1.14	.74	.21
14.2	1.15	.76	.22
14.4	1.17	.76	.22
14.6	1.16	.76	.22
14.8	1.17	.77	.22
15.o	1.17	.78	.22
17.1	-	.83	-
17.4	-	-	.22
18.6	1.23	-	-

GRAPH XIX (Nickel - Tin)

Pressure - 2o tons per sq, in.

Composition - 7o/3o Ni/Sn

Cold junction temperature - 22.o° C

Resistance current - 3.o amp.

A	B	C	A	B	C	A	B	C
.2	3.98	.o21	6.2	4.84	.128	12.2	5.11	.356
.4	4.oo	.o23	6.4	4.9o	.133	12.4	5.12	.363
.6	4.o3	.o24	6.6	4.96	.137	12.6	5.17	.373
.8	4.o5	.o26	6.8	4.97	.142	12.8	5.2o	.388
1.o	4.o8	.o28	7.o	5.o2	.149	13.o	5.23	.392
1.2	4.1o	.o29	7.2	5.o2	.152	13.2	5.31	.4o4
1.4	4.12	.o31	7.4	5.o2	.158	13.4	5.34	.413
1.6	4.14	.o33	7.6	4.98	.161	13.6	5.37	.422
1.8	4.16	.o35	7.8	4.87	.17o	13.8	5.36	.431
2.o	4.17	.o36	8.o	4.83	.172	14.o	5.43	.446
2.2	4.2o	.o39	8.2	4.76	.182	14.2	5.5o	.462
2.4	4.22	.o42	8.4	4.69	.188	14.4	5.59	.478
2.6	4.27	.o45	8.6	4.71	.19o	14.6	5.66	.492
2.8	4.3o	.o47	8.8	4.67	.198	14.8	5.68	.5oo
3.o	4.32	.o51	9.o	4.66	.2o4	15.o	5.71	.519
3.2	4.35	.o53	9.2	4.73	.2o9	15.2	5.76	.538
3.4	4.37	.o57	9.4	4.88	.219	15.4	5.78	.559
3.6	4.41	.o61	9.6	4.93	.229	15.6	5.8o	.573
3.8	4.42	.o67	9.8	4.94	.234	15.8	5.82	.599
4.o	4.45	.o72	1o.o	4.96	.24o	16.o	5.84	.626
4.2	4.5o	.o78	1o.2	5.o2	.268	16.2	5.87	.651
4.4	4.53	.o82	1o.4	5.o3	.281	16.4	5.89	.672
4.6	4.57	.o86	1o.6	5.o4	.293	16.6	5.96	.7o9
4.8	4.59	.o9o	1o.8	5.o7	.293	16.8	6.o2	.741
5.o	4.63	.o94	11.o	5.o9	.3o1	17.o	6.o3	.785
5.2	4.68	.o98	11.2	5.o8	.3o9	17.2	6.o9	.819
5.4	4.7o	.1o3	11.4	5.1o	.316	17.4	6.18	.855
5.6	4.73	.1o9	11.6	5.11	.325	17.6	6.2o	.9o1
5.8	4.75	.116	11.8	5.12	.335	17.8	6.26	.942
6.o	4.8o	.12o	12.o	5.13	.346	18.o	6.28	.987

GRAPH XIX (Copper - Tin)

Pressure - 20 tons per sq. in.

Composition - 85/15 Cu/Sn

Cold junction temperature - 18.°C

A	B	A	B	A	B	A	B
3.5	.54	8.2	.58	13.0	.65	17.8	.71
3.8	.54	8.4	.58	13.2	.66	18.0	.70
4.0	.54	8.6	.59	13.4	.66	18.2	.71
4.2	.54	8.8	.59	13.6	.66	18.4	.71
4.4	.53	9.0	.59	13.8	.66	18.6	.72
4.6	.54	9.2	.58	14.0	.66	18.8	.76
4.8	.54	9.4	.59	14.2	.66	19.0	.77
5.0	.54	9.6	.60	14.4	.67	19.2	.79
5.2	.55	9.8	.61	14.6	.67	19.4	.81
5.4	.54	10.0	.62	14.8	.67	19.6	.91
5.6	.54	10.2	.62	15.0	.67	19.8	.92
5.8	.54	10.4	.62	15.2	.67	20.0	.92
6.0	.53	10.6	.62	15.4	.67	20.2	.93
6.2	.54	10.8	.63	15.6	.67	20.4	.93
6.4	.56	11.0	.63	15.8	.67	20.6	.93
6.6	.56	11.2	.63	16.0	.68	21.2	.96
6.8	.56	11.4	.63	16.2	.68	21.8	.98
7.0	.55	11.6	.63	16.4	.71		
7.2	.56	11.8	.63	16.6	.73		
7.4	.56	12.0	.63	16.8	.73		
7.6	.57	12.2	.63	17.0	.73		
7.8	.58	12.4	.63	17.2	.73		
8.0	.58	12.6	.64	17.4	.74		
		12.8	.65	17.6	.74		

GRAPH XX

Pressure - 2o tons per sq, in.

Composition - 7o/3o Ni/Zn

Cold junction temperature - 21.5°C

Resistance current - 3.o amp.

A	B	C	A	B		A	B	C
.2	4.2o	.o48	6.2	5.15	.181	12.2	7.59	3.22o
.4	4.26	.o54	6.4	5.19	.184	12.4	7.55	3.253
.6	4.3o	.o56	6.6	5.25	.19o	12.6	7.45	3,272
.8	4.33	.o58	6.8	5.29	.193	12.8	7.45	3.27o
1.o	4.36	.o61	7.o	5.32	.2o2	13.o	7.38	3.252
1.2	4.39	.o64	7.2	5.35	.2o5	13.2	7.34	3.241
1.4	4.42	.o66	7.4	5.38	.212	13.4	7.31	3.218
1.6	4.45	.o69	7.6	5.4o	.216	13.6	7.31	3.192
1.8	4.47	.o72	7.8	5.42	.221	13.8	7.36	3.171
2.o	4.49	.o72	8.o	5.48	.232	14.o	7.41	3.162
2.2	4.54	.o75	8.2	5.49	.235	14.2	7.45	3.159
2.4	4.57	.o81	8.4	5.51	.239	14.4	7.49	3.154
2.6	4.58	.o83	8.6	5.5o	.245	14.6	7.53	3.163
2.8	4.6o	.o86	8.8	5.45	.255	14.8	7.52	3.171
3.o	4.64	.o92	9.o	5.42	.258	15.o	7.53	3.199
3.2	4.68	.o95	9.2	5.42	.262	15.2	7.57	3.229
3.4	4.71	.o99	9.4	5.42	.272	15.4	7.58	3.26o
3.6	4.75	.1o2	9.6	5.41	.412	15.6	7.57	3.289
3.8	4.78	.1o9	9.8	5.39	.791	15.8	7.68	3.319
4.o	4.82	.114	1 o.o	5.26	1.o91	16.o	7.69	3.352
4.2	4.87	.119	1o.2	5.2o	.1293	16.2	7.73	3.375
4.4	4.9o	.123	1o.4	5.1o	1.589	16.4	7.85	3.391
4.6	4.93	.128	1o.6	4.93	1.949	16.6	7.88	3.4oo
4.8	4.96	.132	1o.8	4.82	2.361	16.8	7.92	3.4o2
5.o	5.o1	.14o	11.o	5.35	2.815	17.o	8.o1	3.4o8
5.2	5.o3	.148	11.2	6.oo	2.1583 ''	17.2	8.11	3.411
5.4	5.o4	.152	11.4	6.8o	2.463	17.4	8.19	3.412
5.6	5.o8	.159	11.6	7.37	2.755	17.6	8822	3.418
5.8	5.o8	.164	11.8	7.57	3.o39	17.8	8.28	3.42o
6.o	5.1o	.174	12.o	7.61	3.156	18.o	8.39	3.421

'' 1.ooo mm should be added to column C readings above 11.2 mv.

GRAPH XX1 (Differential curves)

Pressure - 20 tons per sq. in.

Composition - A 70/30 Cu/Zn; B 70/30 Ni/Zn.

Cold junction temperature - 21.5°C

mv	A	B	mv	A	B	mv	A	B
0.2	-.024	.000	6.4	.013	.000	12.6	.406	-.039
0.4	-.028	.001	6.6	.016	-.002	12.8	.371	-.032
0.6	.029	.002	6.8	.016	-.003	13.0	.359	-.033
0.8	.029	.003	7.0	.017	-.005	13.2	.358	-.035
1.0	.024	.004	7.2	.025	-.008	13.4	.361	-.036
1.2	.023	.006	7.4	.016	-.010	13.6	.369	-.035
1.4	.021	.007	7.6	.016	-.013	13.8	.385	-.036
1.6	.021	.008	7.8	.019	-.016	14.0	.392	-.035
1.8	.017	.009	8.0	.021	-.017	14.2	.407	-.034
2.0	.013	.010	8.2	.024	-.020	14.4	.422	-.032
2.2	.009	.010	8.4	.028	-.023	14.6	.429	-.031
2.4	.002	.010	8.6	.028	-.028	14.8	.429	-.030
2.6	.000	.010	8.8	.029	-.033	15.0	.436	-.030
2.8	-.004	.010	9.0	.028	-.045	15.2	.435	-.029
3.0	-.009	.010	9.2	.029	-.064	15.4	.429	-.028
3.2	-.013	.010	9.4	.030	-.063	15.6	.416	-.028
3.4	-.013	.009	9.6	.035	-.057	15.8	.402	-.028
3.6	-.009	.008	9.8	.052	-.054	16.0	.383	-.027
3.8	-.009	.008	10.0	.105	-.052	16.2	.379	-.026
4.0	-.008	.007	10.2	.275	-.048	16.4	.370	-.026
4.2	-.005	.006	10.4	.625	-	16.6	.412	-.026
4.4	-.006	.005	10.6	.713	-.045	16.8	.337	-.026
4.6	-.008	.005	10.8	.592	-	17.0	.301	-.024
4.8	-.002	.004	11.0	.525	-	17.2	.274	-.023
5.0	-.001	.004	11.2	.502	-	17.4	.258	-.021
5.2	.000	.003	11.4	.500	-	17.6	.241	-.020
5.4	.001	.003	11.6	.509	-.041	17.8	.227	-.019
5.6	.010	.002	11.8	.532	-.039	18.0	.219	-
5.8	.009	.001	12.0	.543	-.035	18.2	.202	-.021
6.0	.009	.001	12.2	.509	-.035	18.4	.188	
6.2	.010	.000	12.4	.456	-			

Graph XX11

Pressure - 20 tons Atmosphere - Hydrogen

Composition - 70/30 Cu/Zn A - FINES B - AS RECEIVED

Cold junction temperature - 17°C

mv	A	B	mv	A	B	mv	A	B
0.0	-	.01	6.6	.11	.08	11.4	.88	.72.
1.2	108	-	6.8	.11	.07	11.6	.97	.80
1.2	.08	-	7.0	.12	.09	11.8	1.06	.86
1.4	-	-	7.2	.12	.10	12.0	1.22	.97
2.2	.09	-	7.4	.13	.15	12.2	1.35	1.07
2.8	.09	-	7.6	.14	.18	12.4	1.46	1.22
3.0	.09	-	7.8	.19	.20	12.6	1.60	1.38
3.2	.08	-	8.0	.25	.24	12.8	1.98	1.56
3.4	.08	-	8.2	.31	.27	13.0	2.21	1.74
3.6	.08	-	8.4	.34	.29	13.2	2.41	1.81
3.8	.08	-	8.6	.37	.31	13.4	2.58	2.06
4.0	.09	-	8.8	.38	.32	13.6	2.69	2.23
4.2	.08	.03	9.0	.41	.34	13.8	2.81	2.36
4.4	.07	.03	9.2	.43	.36	14.0	2.90	2.48
4.6	.08	-	9.4	.46	.38	14.2	2.98	2.59
4.8	.09	.06	9.6	.49	.41	14.4	3.00	2.69
5.0	.08	.06	9.8	.53	.43	14.6	3.03	2.75
5.2	.08	.06	10.0	.56	.47	14.8	3.05	2.83
5.4	.09	.07	10.2	.62	.50	15.0	3.08	2.89
5.6	.09	.06	10.4	.66	.52	15.2	3.09	2.93
5.8	.08	.06	10.6	.68	.56	15.4	3.12	2.96
6.0	.09	.06	10.8	.71	.58	15.6	3.13	2.99
6.2	.09	.07	11.0	.76	.63	15.8	3.15	3.03
6.4	.11	.07	11.2	.82	.67	16.0	3.17	3.05
						18.2	-	3.22